

Catalysis and Catalytic Reactions

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Adsorption isotherms

Langmuir Isotherm

$$\frac{P}{x/m} = \frac{1}{k_1 k_2} + \frac{P}{k_2}$$

p = gas pressure

x = amount of gas adsorbed by definite mass (m)

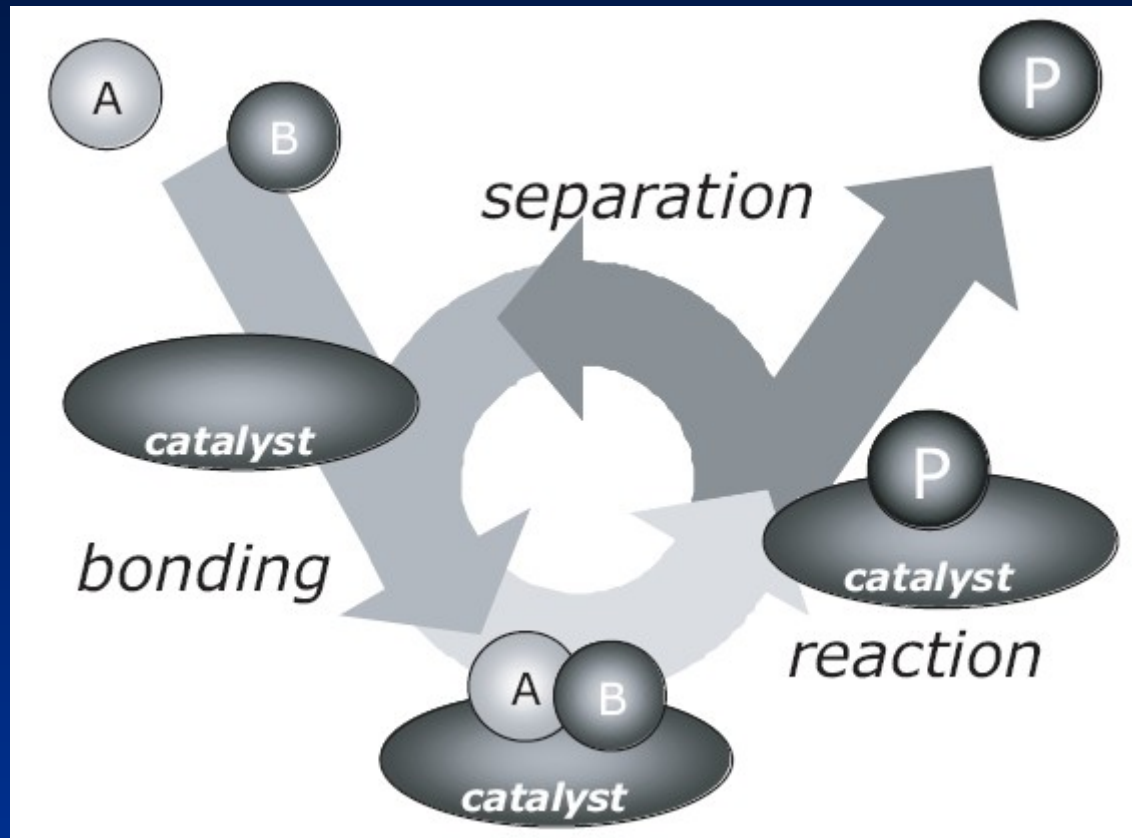
k_1 & k_2 are constants

Scope:

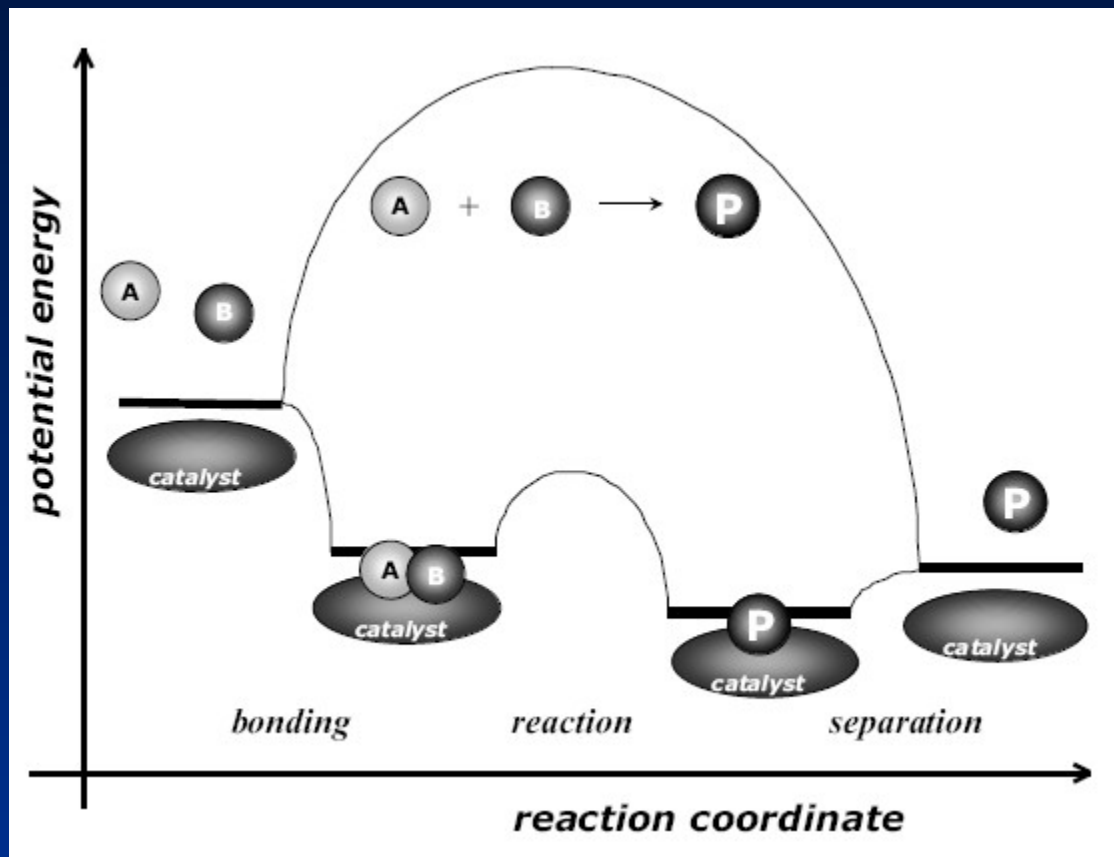
- Catalyst & Catalysis ??
- Our subject is limited to gas phase reactions catalyzed by solids
- ***Physical*** properties of catalysts
- Mechanism & rate laws
- Interpretation of data – estimation of rate law parameters
- Catalytic reactors

What is a catalyst ??

- Alters the rate of reaction
- Highly selective
- Does it participate in the reaction ??
- How does it change the rate ?? – Offers an alternate path with low E.
- Does it affect ΔH_R , ΔG_R , and Equilib. constant ??
- Does it affect yield & selectivity ??
- Does it initiate a reaction ??



Every catalytic reaction is a sequence of ***elementary*** steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle



Potential energy diagram of a heterogeneous catalytic reaction, with gaseous reactants and products and a solid catalyst. Note that the uncatalyzed reaction has to overcome a substantial energy barrier, whereas the barriers in the catalytic route are much lower.

Example: *Boudart* compared the homogeneous versus catalytic rates of ethylene hydrogenation.

Homogeneous reaction:

$$r = 10^{27} \exp\left(-\frac{43000}{RT}\right) p_{H_2}$$

Catalytic – same above reaction:

$$r = 2 \times 10^{27} \exp\left(-\frac{13000}{RT}\right) p_{H_2}$$

At 600 K the ratio of catalytic to homogeneous rate is 1.44×10^{11}

What is a catalyst ??

- As old as civilisations, catalysts were in use for making wine, cheese etc.
- Small amounts of catalyst required
- Efficiency depends on activity, properties & life of the catalyst
- Examples:
 - Ammonia synthesis – Promoted iron
 - SO₂ oxidation – Vanadium Pentaoxide
 - Cracking – Silica, alumina
 - Dehydrogenation – Platinum, Molybdenum

CHEMOSORPTION ABILITIES

	O ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂	CO ₂	N ₂
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co,	+	+	+	+	+	+	-
Pd, Pt,	+	+	+	+	+	-	-
Mn, Cu,	+	+	+	+	±	-	-
Al, Au	+	+	+	+	-	-	-
Li, Na, K	+	+	-	-	-	-	-
Mg, Ag, Zn, Pd	+	-	-	-	-	-	-

Catalysts are very specific towards chemical reactions

Classification:

- Homogenous catalysis: the catalyst and reacting substances are in the same physical state
- e.g. esterification of ethanol by acetic acid in the presence of H_2SO_4 .----homogeneous
- Heterogeneous catalysis $H_2 + O_2 \xrightarrow{Pt\ powder} H_2O$

Catalysts are generally used to:

- Speedup reactions
- Change the operating temperature level
- Influence the product distribution

Definitions

**Please do note the
differences between
their action**

Promoter: is an additive which has no catalytic properties of its own but enhances the activity of a catalyst

Promoter results in all or some of the following:

- Increase of ***available surface area***
- Stabilization against crystal growth and sintering
- Improvement of mechanical strength

Examples: Alumina, Asbestos

Carrier: principally serve as a framework on which catalyst is deposited - no catalytic properties of its own but may take part in physical adsorption.

Carrier results in:

- Highly porous nature - increase of available surface area
- Improve stability
- Improves the heat transfer characteristics

Examples: Alumina, Asbestos, Carborundum, Iron oxide, Manganese, Activated carbon, Zinc oxide

Accelerator: are substances which can be added to a reacting system to maintain the activity of a catalyst by **nullifying** the effects of poisons

Poisons: substances which reduce the activity of a catalyst. They are not deliberately added but are unavoidably deposited during the reaction

Examples: Sulfur, Lead, Metal ions such as Hg, Pd, Bi, Sn, Cu, Fe etc.

Inhibitor: substances added to the catalyst during its manufacture to reduce its activity.

Coking/Fouling: deposition of carbonaceous material on the surface of the catalyst - Common to reactions involving hydrocarbons

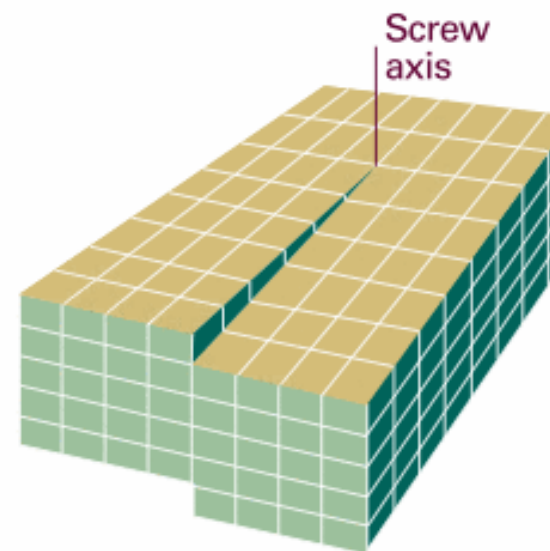
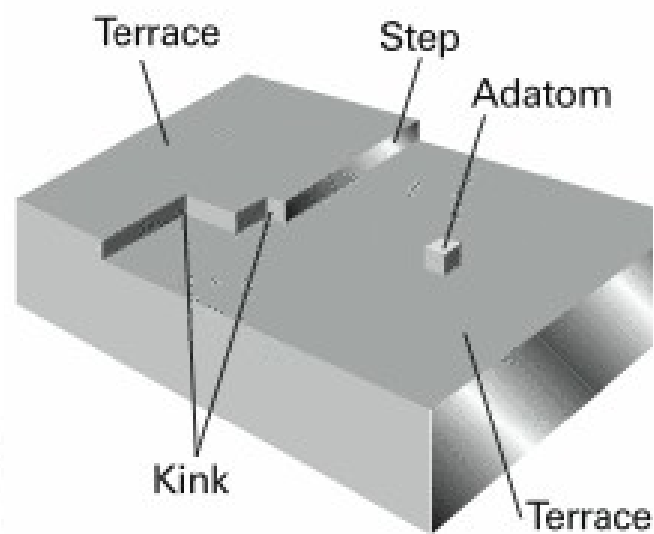
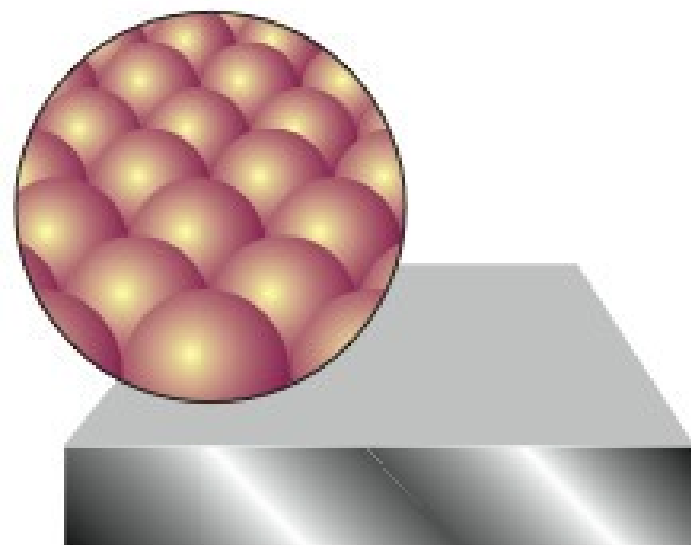
Activity: of a catalyst depends on the texture and electronic structure.
Activity of a catalyst can be explained by:

- Active centers on the surface of the catalyst
- Geometry of surface
- Electronic structure
- Formation of surface intermediates

Efficiency of a catalyst depends on :
Activity, Selectivity and Life

Active site: is a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom/molecule. These sites are **unsaturated atoms** in the solid resulting from:

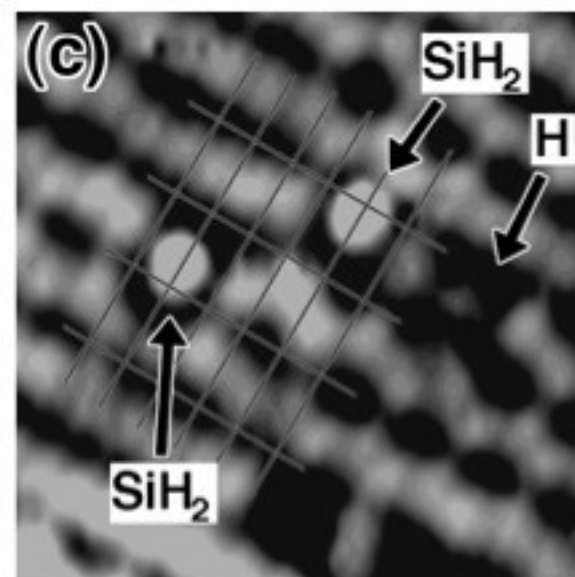
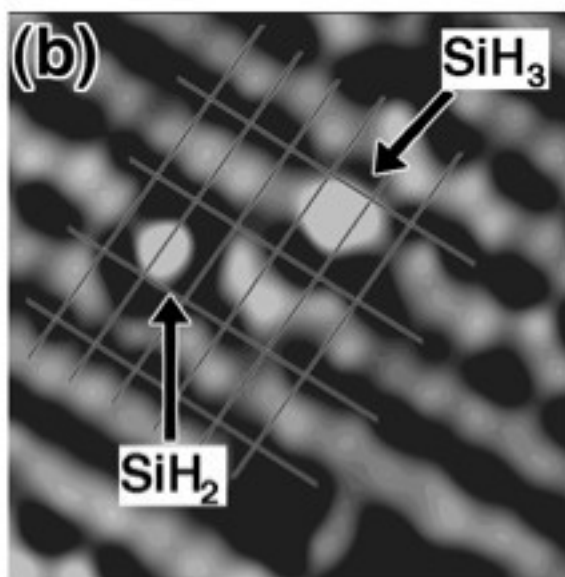
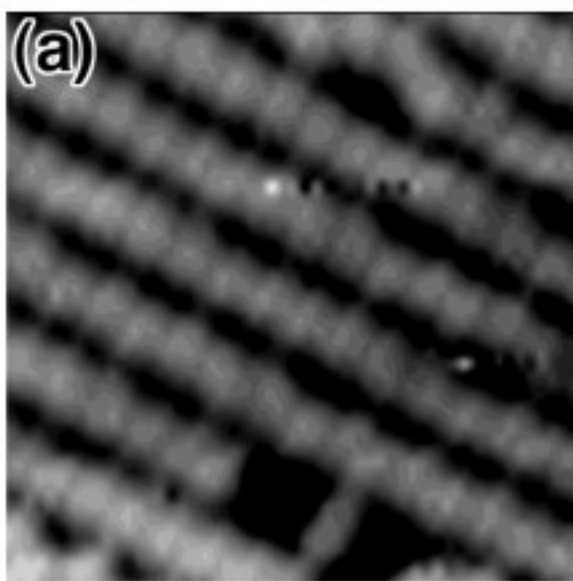
- Surface irregularities
- Dislocations
- Edges of crystals
- Cracks along grain boundaries



- Visualization by STM of the reaction



on a $4.7 \text{ nm} \times 4.7 \text{ nm}$ area of a Si(001) surface. (a) The Si(001) surface before exposure to $\text{Si}_2\text{H}_6(\text{g})$. (b) Adsorbed Si_2H_6 dissociates into $\text{SiH}_2(\text{surface})$, on the left of the image, and $\text{SiH}_3(\text{surface})$, on the right. (c) After 8 min, $\text{SiH}_3(\text{surface})$ dissociates to $\text{SiH}_2(\text{surface})$ and $\text{H}(\text{surface})$.



Adsorption

- Adsorption is a process in which a substance becomes attached to the surface of a solid or a liquid.
- Absorption in which the substance becomes distributed throughout the solid or liquid.
- The substances adsorbed on the surface of a solid could be gases, liquids or other solids (from solution). The amount of material adsorbed by a given mass of adsorbent depends on the physical state of the latter, most materials being adsorbed when the solid is porous or finely divided. This confirms that adsorption is a surface phenomenon.

Types of adsorption

- Adsorption can be either a physical (physisorption) process or a chemical process (chemisorption), or both at the same time.
- In physical adsorption –weak forces are involved , mainly Van der Waals forces or hydrogen bonding. The amount of the gas adsorbed increases with a decrease in T.
- Chemisorption is due to the existence on the adsorbent of unsatisfied valencies whereby molecules or ions of another substance become attached to the surface atoms or ions of the solid. The attachment takes place via covalent or ionic bonds

Application of adsorption & where adsorption

Application of adsorption

1. Adsorption indicators
2. Chromatography
3. Purification of organic compounds
4. “Decolorizing” of sugar
5. Medicines

Where adsorption takes place?

*At active sites
which could be :*

- Dislocations
- Steps
- Skew areas
- Missing atoms
and so on

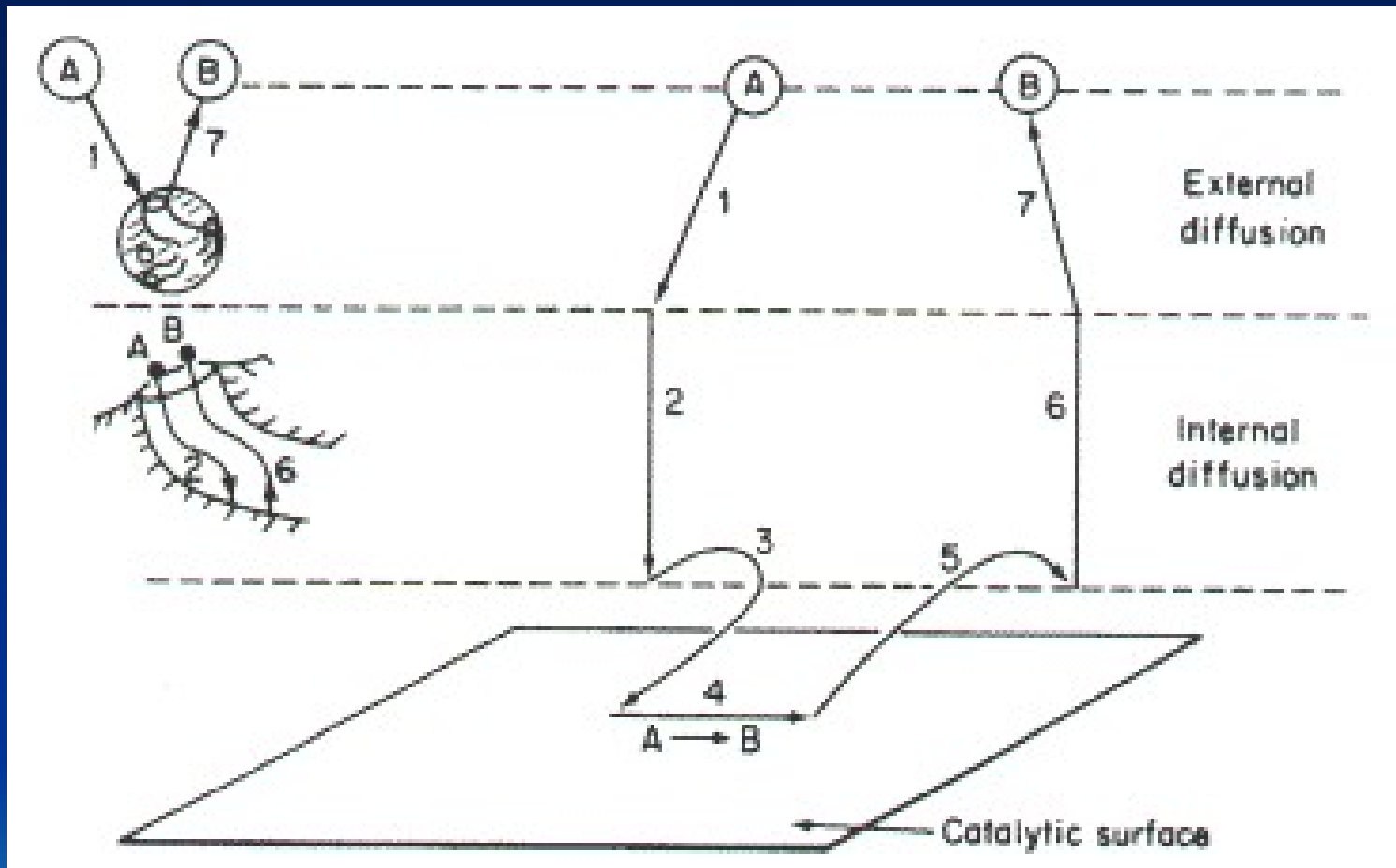
Historical development of kinetics in relation to catalysis

1813	Thénard	Ammonia decomposition on several metals
1814	Kirchhoff	Hydrolysis of starch catalyzed by acids
1817	Humphrey Davy	Mixture of coal gas and air makes platinum wire white hot
1818	Thénard	Measurements on rate of H_2O_2 decomposition
1823	Döbereiner	Selective oxidation of ethanol to acetic acid on platinum
1834	Faraday	Comprehensive description of $\text{H}_2 + \text{O}_2$ reaction on platinum
1835	Berzelius	Definition of catalysis, catalyst, catalytic force
1850	Wilhelmy	First quantitative analysis of reaction rates
1862	Guldberg & Waage	Law of mass action
1865	Harcourt & Esson	Systematic study on concentration dependence of reaction rate
1884	Van 't Hoff	First concise monograph on chemical kinetics
1887	Ostwald	Definition of order of a reaction
1889	Arrhenius	Arrhenius equation: $k = \nu \exp(-E_a/k_B T)$
1905	Nernst	Third law of thermodynamics
1908	Haber	Prediction of conditions for ammonia synthesis
1913	Chapman	Steady state approximation
1915	Langmuir	Quantitative theory of adsorption of gases on surfaces
1921	Lindemann	Mechanism of unimolecular reactions – activation by collisions
1925	Taylor	Catalytically active sites on surfaces
1927	Hinshelwood	Kinetic mechanism of reactions in heterogeneous catalysis
1931	Onsager	Non-equilibrium thermodynamics
1935	Eyring; Polanyi & Evans	Transition-state theory

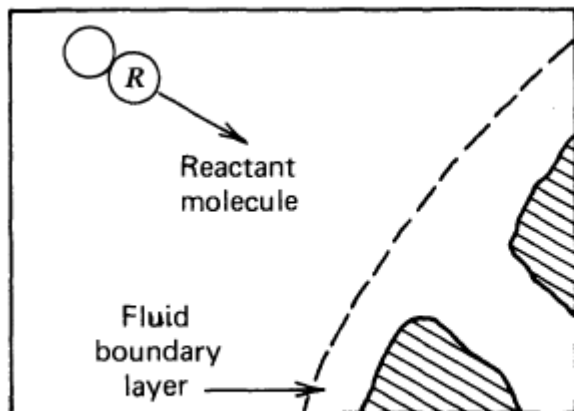
Mechanism of Heterogeneous Catalysis:

1. Bulk Diffusion of reacting molecules to the surface of the catalyst
2. Pore Diffusion of reacting molecules into the interior pores of the catalyst
3. Adsorption of reactants (chemisorption) on the surface of the catalyst
4. Reaction on the surface of the catalyst between adsorbed molecules
5. Desorption of products
6. Pore Diffusion of product molecules to the surface of the catalyst
7. Bulk Diffusion of product molecules

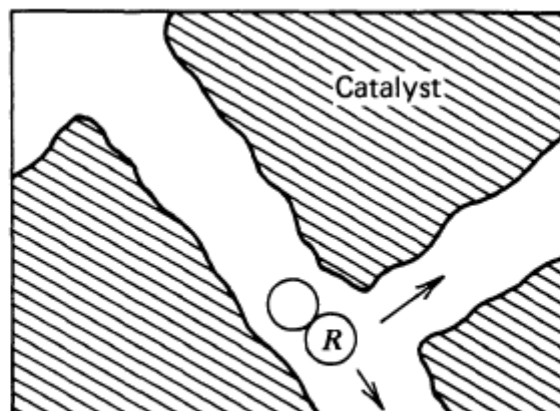
Mechanism of Heterogeneous Catalysis:



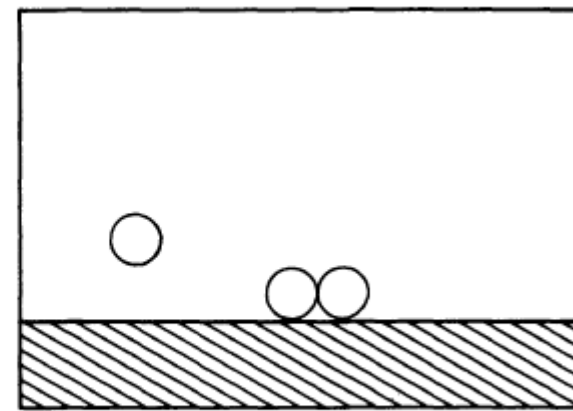
Mechanism of Heterogeneous Catalysis:



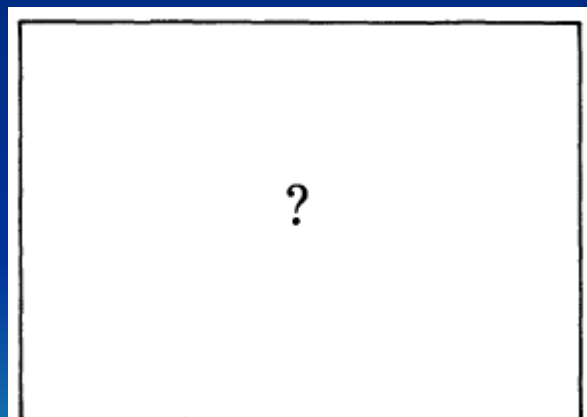
1. Mass transfer through external boundary layer



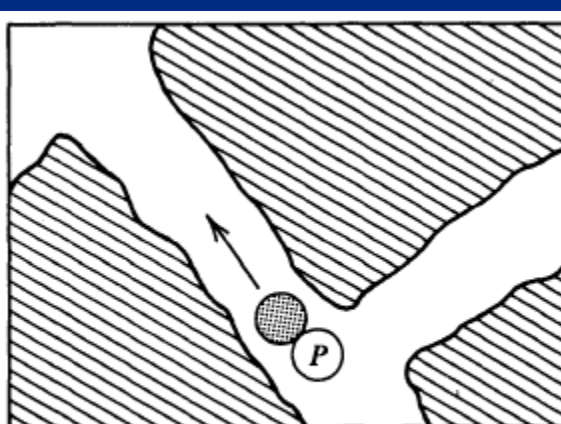
2. Diffusion into pores



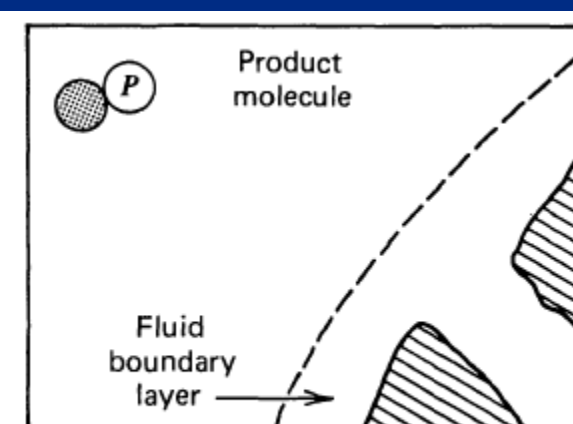
3. Chemisorption



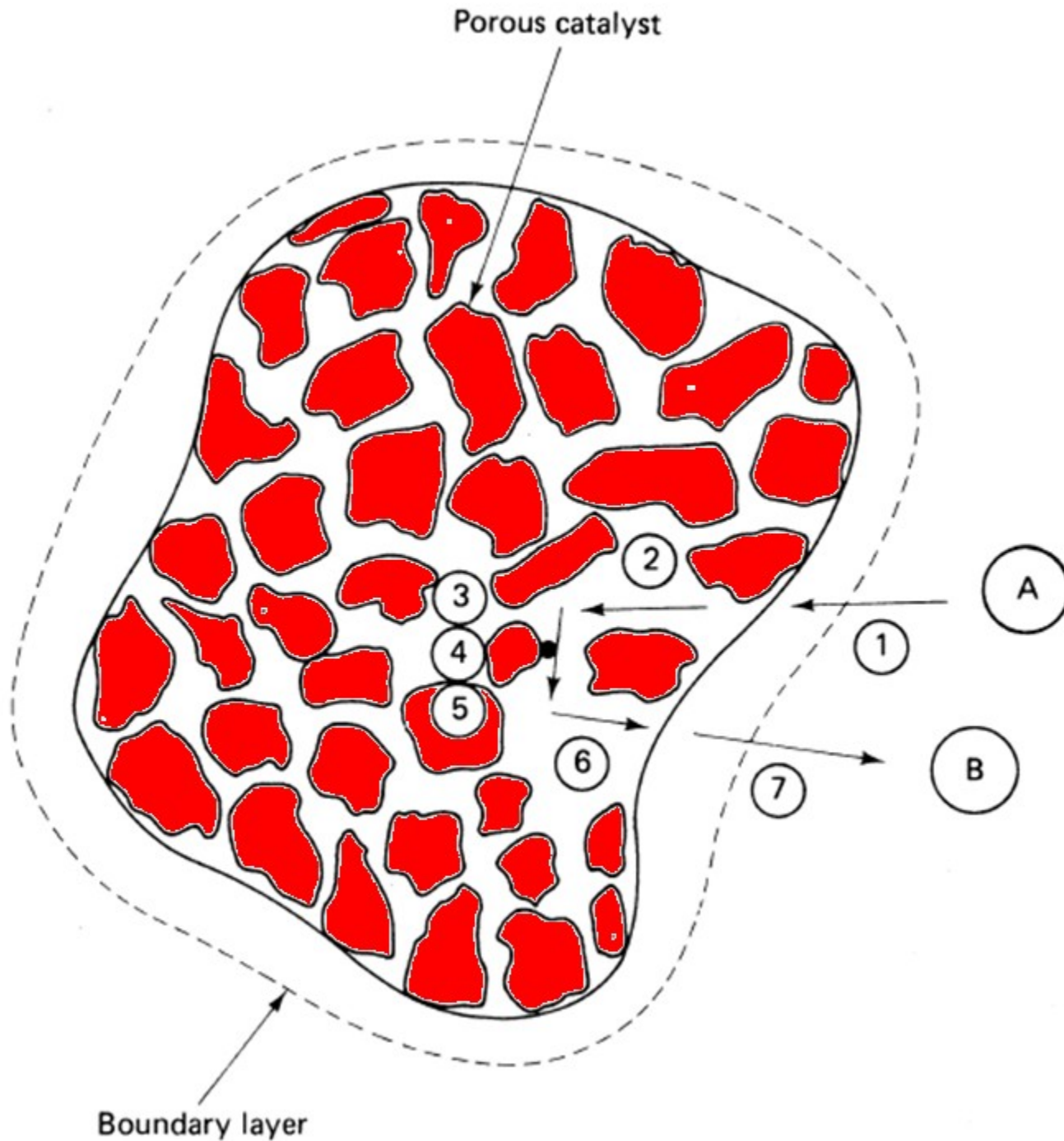
4,5 Reaction and desorption of products



6. Diffusion of products out of pores

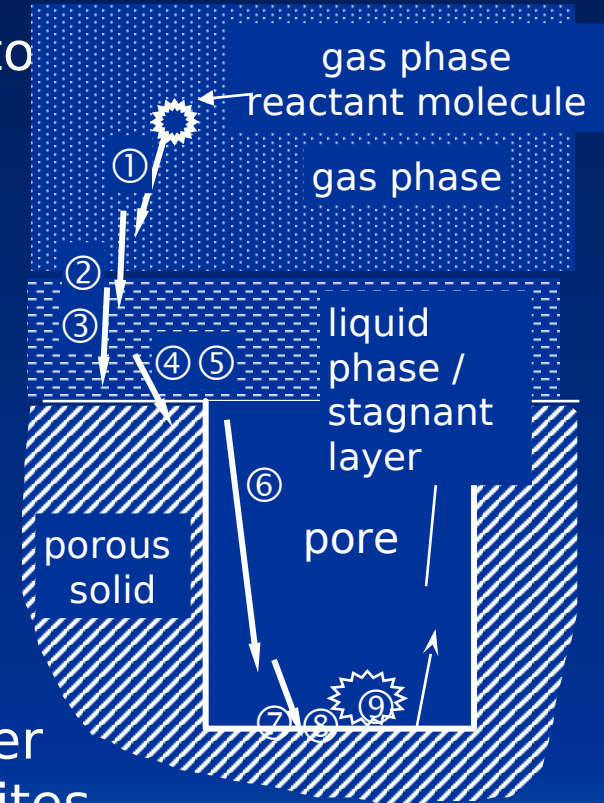


7. Mass transfer back to bulk fluid

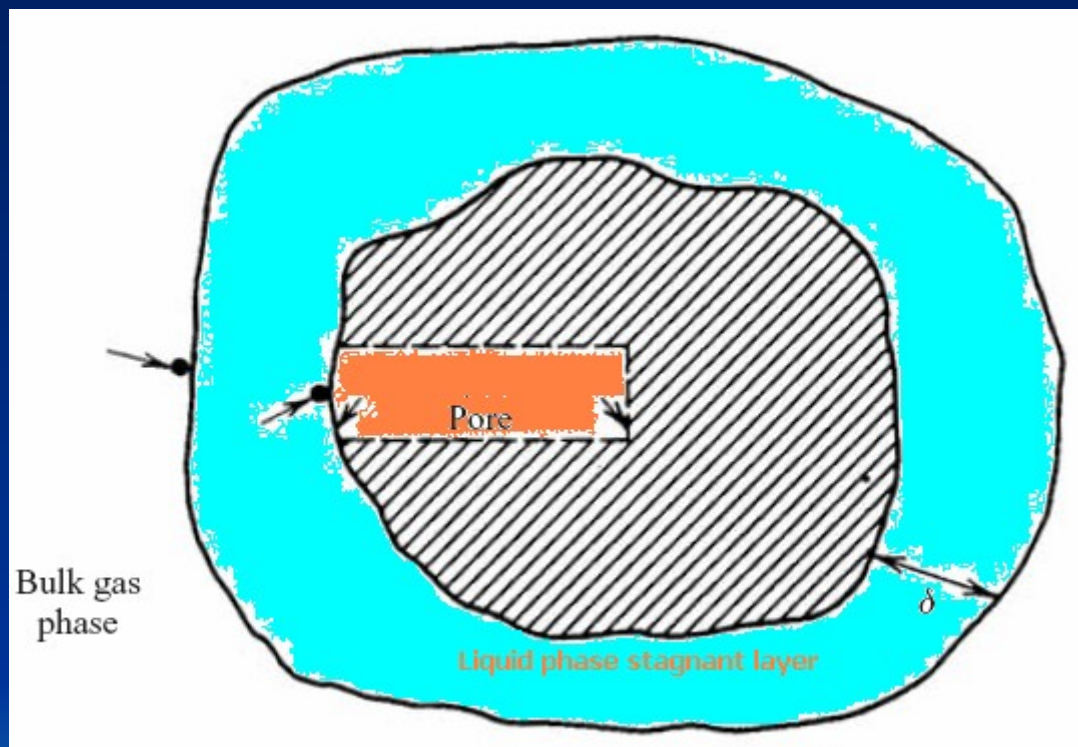


Example Heterogeneous Catalytic Reaction Process

- The long journey for reactant molecules to
 - 1. travel within gas phase
 - 2. cross gas-liquid phase boundary
 - 3. travel within liquid phase/stagnant layer
 - 4. cross liquid-solid phase boundary
 - 5. reach outer surface of solid
 - 6. diffuse within pore
 - 7. arrive at reaction site
 - 8. be adsorbed on the site and activated
 - 9. react with other reactant molecules, either being adsorbed on the same/neighbour sites or approaching from surface above
- Product molecules must follow the same track in the reverse direction to return to gas phase
- Heat transfer follows similar track



Pore and film resistances in a catalyst particle



Solid Catalysts

- Catalyst composition

- Active phase

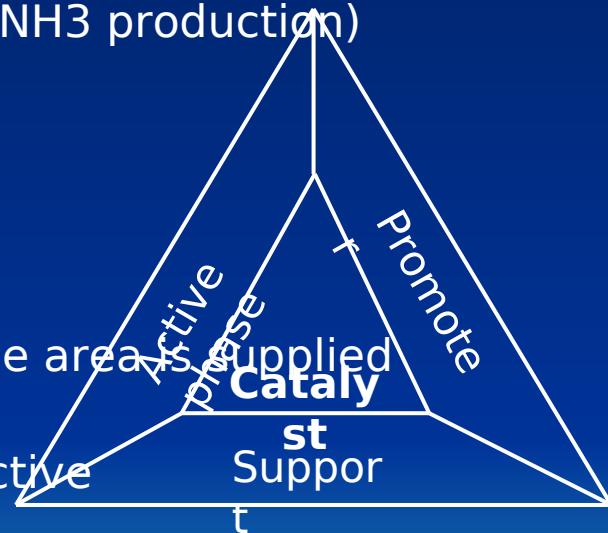
- Where the reaction occurs (mostly metal/metal oxide)

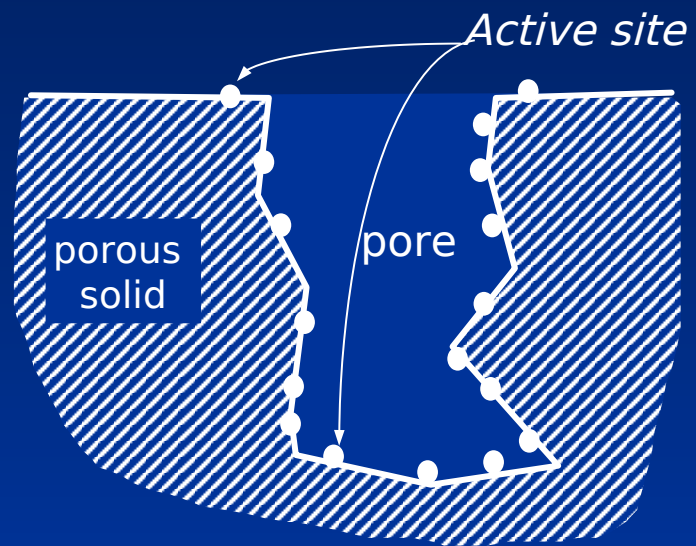
- Promoter

- Textual promoter (e.g. Al - Fe for NH₃ production)
 - Electric or Structural modifier
 - Poison resistant promoters

- Support / carrier

- Increase mechanical strength
 - Increase surface area (98% surface area is supplied within the porous structure)
 - may or may not be catalytically active





Rate-Determining Step (rds)

In a kinetics scheme involving more than one step, it may be that one change occurs much faster or much slower than the others (as determined by relative magnitudes of rate constants).

In such a case, the overall rate, may be determined almost entirely by the slowest step, called the rate-determining step (rds).

The rate of the rds is infinitesimal when compared to the rates of other steps.

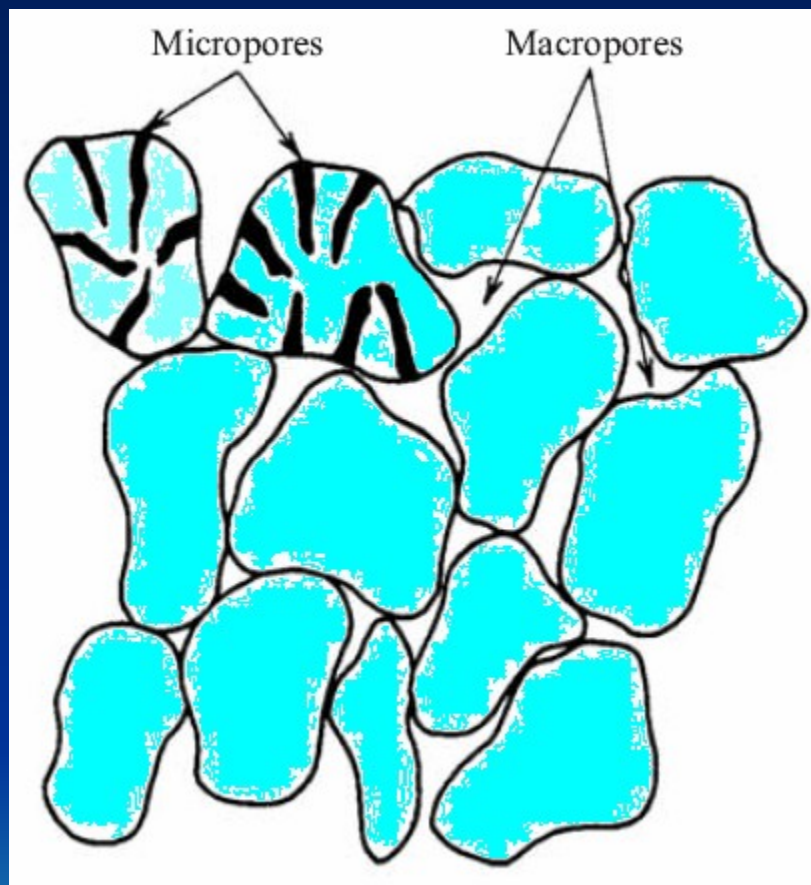
Alternately the rates of other steps are infinite compared to the rate of rds.

Bulk Diffusion:

- Diffusion controlled reactions are usually fast
- Design of reactors – design of mass transfer equipment
- Increase in mass velocity increases the rate
- High L/D ratio reactors (narrow) are favored

Pore Diffusion:

- Pore diffusion controlled reactions are few
- Design of reactors – most complicated
- Approaches bulk diffusion if the pore size is large
- Approaches Knudsen diffusion if the pore size is small.
- No effect of temperature or mass velocity
- Low L/D ratio reactors (wide) may be used with consequent reduction in pressure drop



Chemisorption:

- Chemisorption controlled reactions are usually fast
- Rate increases rapidly with increase in temp.
- Permits the use of wide reactors

Surface reaction:

- 70% of the reactions which are not controlled by diffusion falls under this case
- Rate increases rapidly with increase in temp.

Desorption:

- Desorption of a product could also be rate controlling in a few cases

Complexities:

- Theoretically more than one step can be rate controlling
- Too many possible mechanisms
- Experimental data is normally fitted to any single rate controlling step, which is then called the most plausible mechanism

Physical Adsorption Vs. Chemisorption

Item	Physical Adsorption	Chemisorption
Forces of attraction	Weak - VanderWaals forces	Strong valency forces
Specificity	Low	High
Quantity	Large	Small
Heat Effects	Exothermic, 1-15 kCal/mol	Exothermic, 10-100 kCal/mol
Activation energy	Low	High
Effect of Temp.	Rapid at low temperatures & reach equilibrium quickly. Beyond T_c of the gas, no ads.	Slow at low temp., Rate increases with temp.
Effect of Pressure	Increases with increase in pressure	Little effect
Surface	Whole surface active	Fraction of surface only
Layers	Multi-layer adsorption	Mono-layer adsorption

Chemisorption rates:

- Adsorption data is reported in the form of isotherms
- Chemisorption may be considered as a reaction between a reactant molecule and an active site resulting in an adsorbed molecule

$A + \sigma \rightleftharpoons A\sigma$ (or) $A + S \rightleftharpoons AS$
Turnover Frequency (N): defined as the number of molecules reacting per active site per second at the conditions of the experiment – a measure for the activity of the catalyst

Langmuir Isotherm - Assumptions:

- Surface is uniformly active
- All sites are identical
- Amounts of adsorbed molecules will not interfere with further adsorption
- Uniform layer of adsorption

$$\theta_v = \text{Fraction of vacant sites} = \frac{\text{No of vacant sites}}{\text{total sites}} = \frac{\sigma_v}{\sigma_t}$$

$$\theta_A = \text{Fraction of sites occupied by A} = \frac{\text{No of occupied sites}}{\text{total sites}} = \frac{\sigma_A}{\sigma_t}$$

$$\theta_v + \theta_A = 1$$

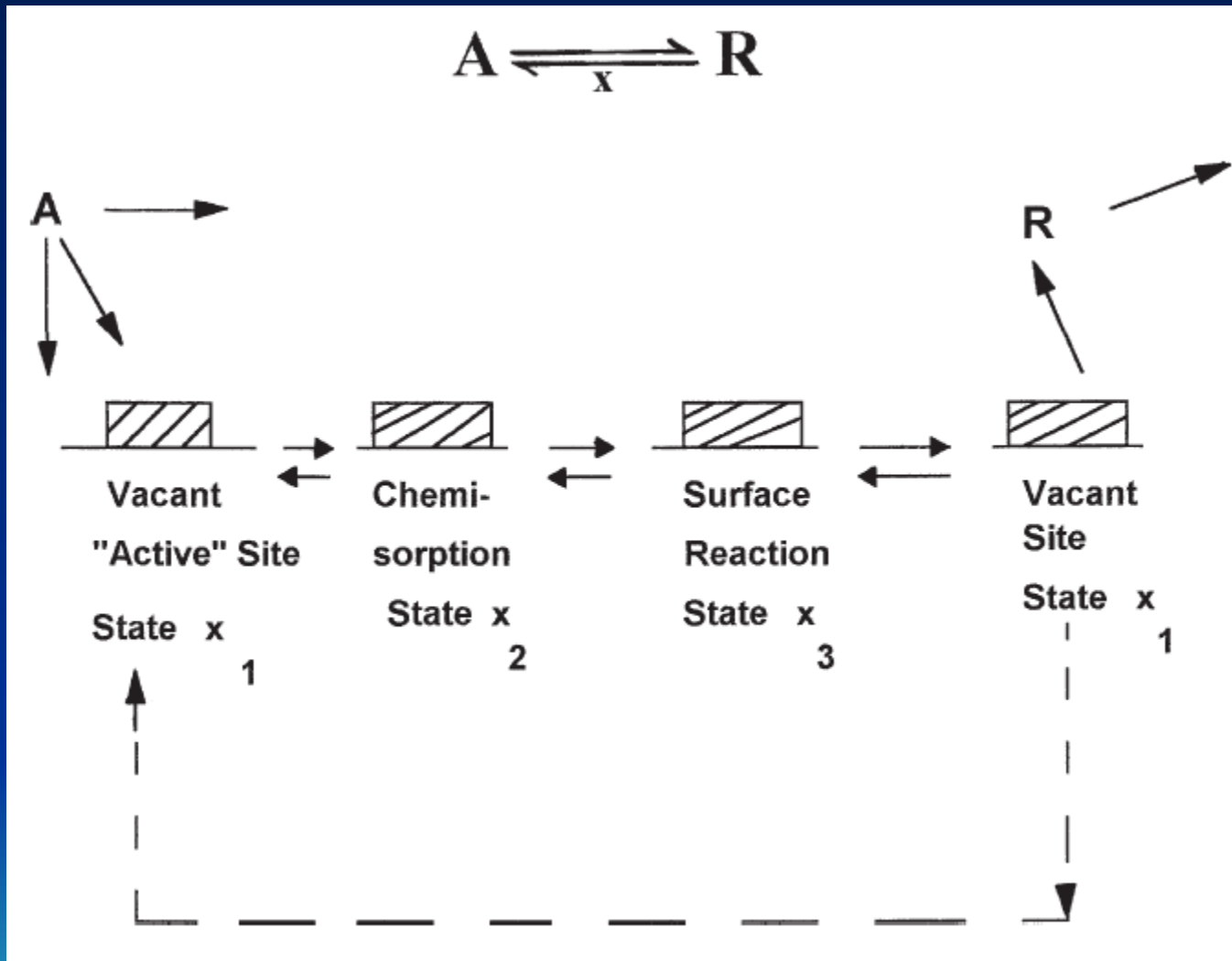
Alternately:

$$C_t = \text{Molar conc of active sites} = \frac{\text{No of active sites/unit mass}}{\text{Avogadro number}}$$

$$C_v = \text{Molar conc of vacant sites} = \frac{\text{No of vacant sites/unit mass}}{\text{Avogadro number}}$$

$$C_{AS} = \text{Molar conc of sites by A} = \frac{\text{No of sites by A/unit mass}}{\text{Avogadro number}}$$

Though $C_t + C_{AS} = C_v$ other isotherms account for non-uniform surfaces, they have primarily been developed for single adsorbing components. Thus, the extensions to interactions in multi-component systems is not yet possible, as with the Langmuir isotherm. Langmuir isotherms are only used for developing kinetic rate expressions. However, not all adsorption data can be represented by a Langmuir isotherm.



Chemisorption rates (molecular adsorption):



$$\text{Forward rate} = k_1 p_A \theta_v$$

$$\text{Backward rate} = k_2 \theta_A$$

At equilibrium: $k_1 p_A \theta_v = k_2 \theta_A$

$$(k_1/k_2) p_A \theta_v = \theta_A$$

$$\theta_v + \theta_A = 1$$

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$$

$$C_{AS} = \frac{K_A p_A C_t}{1 + K_A p_A}$$

Chemisorption rates (Atomic adsorption):



$$\text{Forward rate} = k_A p_A \theta_v^2$$

$$\text{Backward rate} = k_{-A} \theta_A^2$$

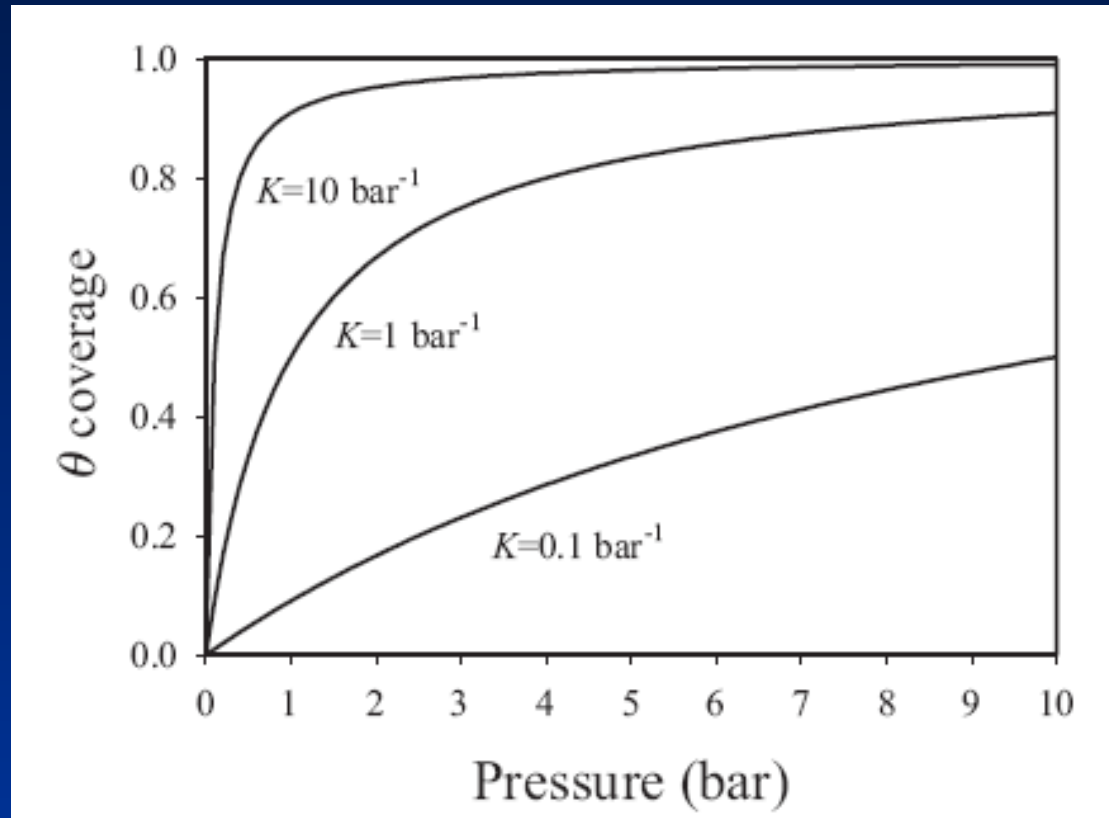
$$\text{At equilibrium: } k_A p_A \theta_v^2 = k_{-A} \theta_A^2$$

$$(k_A/k_{-A}) p_A \theta_v^2 = \theta_A^2$$

$$\theta_A = \frac{\sqrt{K_A p_A}}{1 + \sqrt{K_A p_A}}$$

$$C_{AS} = \frac{\sqrt{K_A p_A}}{1 + \sqrt{K_A p_A}} C_t$$

What would be θ_A if chemisorption does not reach equilibrium ?



Langmuir adsorption isotherm for associative adsorption for three values of the equilibrium constant, K

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$$

Surface Reaction: reaction between the adsorbed molecules on the surface of the catalyst may proceed in a number of ways:

Single site mechanism: $A_{\sigma} \rightleftharpoons R_{\sigma}$

Dual site mechanism: $A_{\sigma} + \sigma \rightleftharpoons R_{\sigma} + \sigma$



Langmuir-Hinshelwood kinetics

Applications of Catalysis

- Environmental applications
 - Pollution controls in combination with industrial processes
 - Pre-treatment - reduce the amount waste/change the composition of emissions
 - Post-treatments - once formed, reduce and convert emissions
 - Using alternative materials
 - ...
 - Pollution reduction
 - gas - converting harmful gases to non-harmful ones
 - liquid - de-pollution, de-odour, de-colour etc
 - solid - landfill, factory wastes
 - ...
 - And many more ...
- Other applications
 - Catalysis and catalysts play one of the key roles in new technology development.

- **General requirements for a good catalyst**
 - **Activity** - being able to promote the rate of desired reactions
 - **Selective** - being to promote only the rate of desired reaction and also retard the undesired reactions
 - **Note:** The selectivity is sometime considered to be more important than the activity and sometime it is more difficult to achieve (e.g. selective oxidation of NO to NO₂ in the presence of SO₂)
 - **Stability** - a good catalyst should resist to deactivation, caused by
 - the presence of impurities in feed (e.g. lead in petrol poison TWC.
 - thermal deterioration, volatility and hydrolysis of active components
 - attrition due to mechanical movement or pressure shock
 - **A solid catalyst should have reasonably large surface area needed for reaction (active sites).** This is usually achieved by making the solid into a porous structure.

Examples of heterogeneous catalysis

The hydrogenation of a carbon-carbon double bond

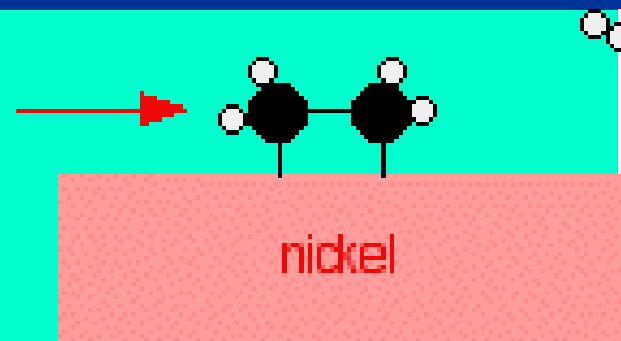
- The simplest example of this is the reaction between ethene and hydrogen in the presence of a nickel catalyst.



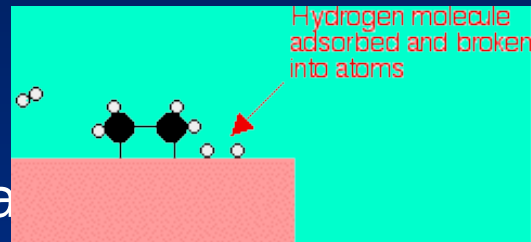
- In practice, this is a pointless reaction, because you are converting the extremely useful ethene into the relatively useless ethane. However, the same reaction will happen with any compound containing a carbon-carbon double bond.

- One important industrial use is in the hydrogenation of vegetable oils to make margarine, which also involves reacting a carbon-carbon double bond in the vegetable oil with hydrogen in the presence of a nickel catalyst.
- Ethene molecules are adsorbed on the surface of the nickel. The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface.

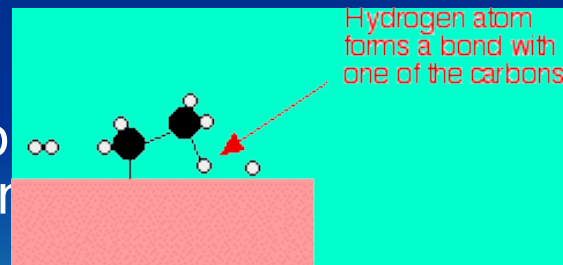
Ethene molecule
adsorbed to the
surface of the metal



- Hydrogen molecules are also adsorbed on to the surface of the nickel. When this happens, the hydrogen molecules are broken into atoms. These can move around on the surface of the nickel.

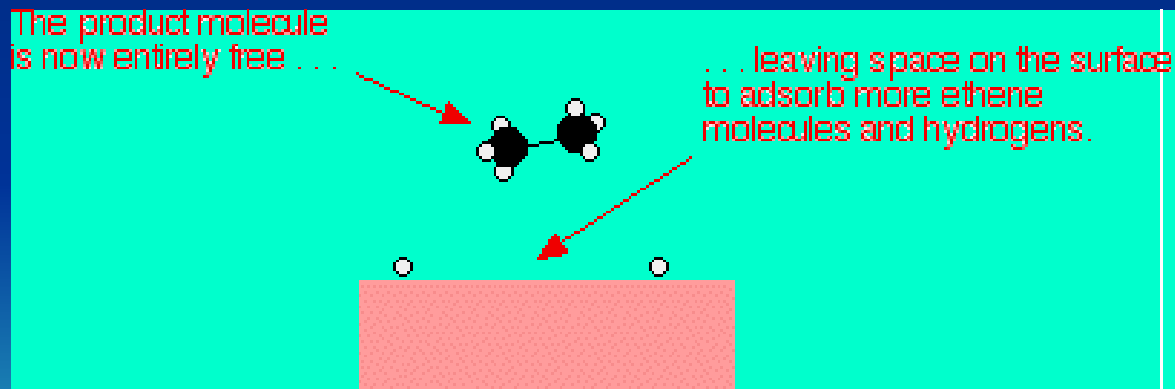


- If a hydrogen atom bonds to one of the bonded carbons, the bond between the carbon and the nickel is replaced by one between the carbon and hydrogen.



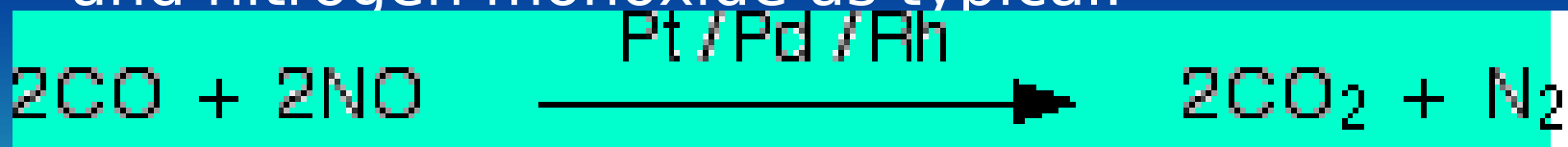
- That end of the molecule breaks free of the surface, and eventually the other end.

- As before, one of the hydrogen atoms forms a bond with the carbon, and that end also breaks free. There is now space on the surface of the nickel for new reactant molecules to go through the whole process again.



Catalytic converters

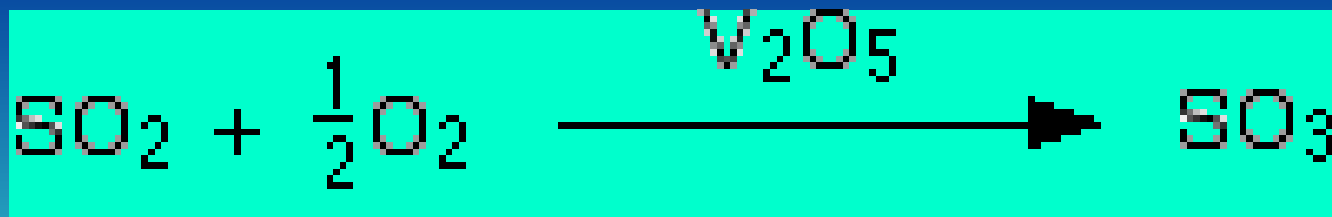
- Catalytic converters change poisonous molecules like carbon monoxide and various nitrogen oxides in car exhausts into more harmless molecules like carbon dioxide and nitrogen. They use expensive metals like platinum, palladium and rhodium as the heterogeneous catalyst.
- The metals are deposited as thin layers onto a ceramic honeycomb. This maximises the surface area and keeps the amount of metal used to a minimum.
- Taking the reaction between carbon monoxide and nitrogen monoxide as typical:



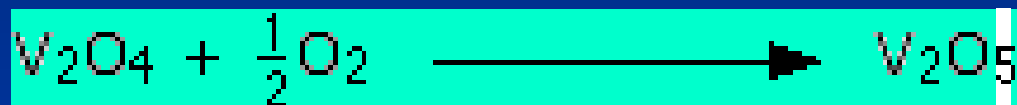
Industrial Application of heterogeneous catalysts.

The use of vanadium (V) oxide in the Contact Process

- During the Contact Process for manufacturing sulphuric acid, sulphur dioxide has to be converted into sulphur trioxide. This is done by passing sulphur dioxide and oxygen over a solid vanadium(V) oxide catalyst



- The sulphur dioxide is oxidised to sulphur trioxide by the vanadium(V) oxide. In the process, the vanadium(V) oxide is reduced to vanadium(IV) oxide.
- The vanadium(IV) oxide is then re-oxidised by the oxygen.



Physical properties of catalysts:

- Bulk density
- Surface area
- Pore volume
- Pore size distribution

For Silica-Alumina catalyst:

Surface area = 200 – 500 m²/gm

Pore volume = 0.2 – 0.7 ml/gm

Measurement of Surface area:

Measuring the surface area active for chemisorption is difficult because of:

- highly selective nature
- fraction of surface
- physical adsorption + chemisorption
- presence of promoter, carrier etc.

Universally surface area of a catalyst is measured using physical adsorption principles. It is approximated that the more the area the more would be the activity of the catalyst.

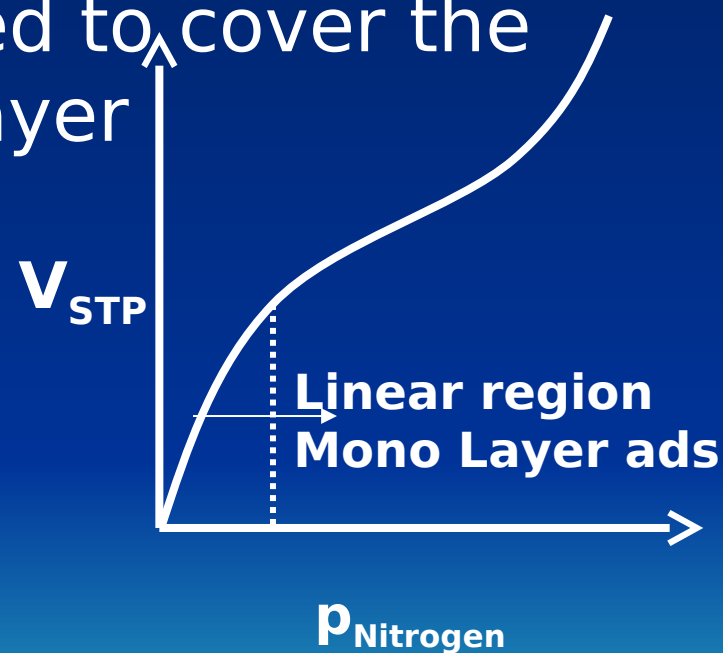
Experiment:

- The amount of N_2 adsorbed at equilibrium at the normal boiling point temp (-195.8°C) is measured over a wide range of N_2 partial pressures below 1 atm.
- Identify the amount required to cover the entire surface by a mono-layer

$p/p_0 < 0.1$ – Mono layer

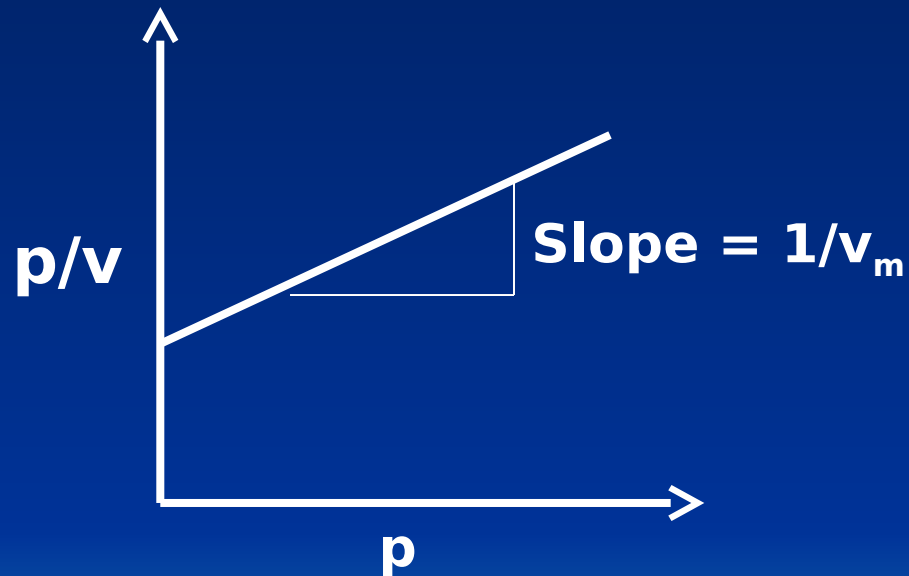
$0.1 < p/p_0 < 0.4$ – Multi layer

$0.4 < p/p_0 < 1.0$ – Capillary condensation



1. Langmuir Isotherm:

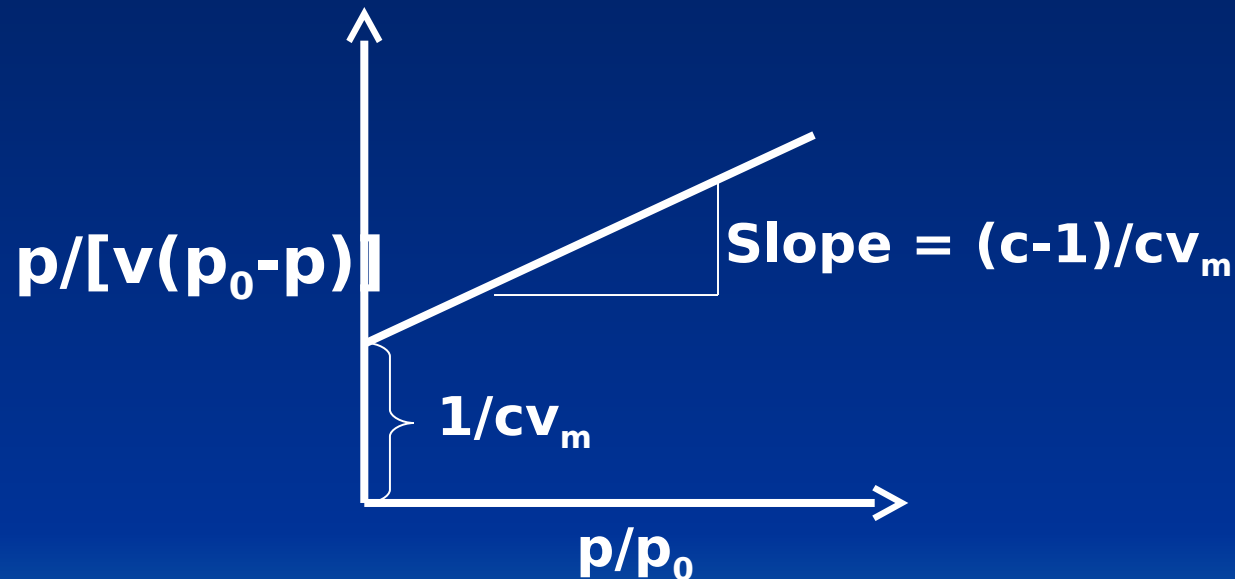
$$\theta_{N_2} = \frac{Kp_{N_2}}{1 + Kp_{N_2}} = \frac{v}{v_m} \Rightarrow \frac{p}{v} = \frac{1}{Kv_m} + \frac{p}{v_m}$$



2. BET Isotherm:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c-1)p}{c v_m p_0}$$

P_0 = vapor pressure / Satn pressure



$$v_m = 1/(\text{slope} + \text{Intercept})$$

- Convert v_m to no. of molecules
- α = area covered by one molecule

$$S = \left(\frac{v_m N_0}{22400} \right) \alpha \quad \alpha = 1.09 \left(\frac{M}{N_0 \rho} \right)^{2/3}$$

- For Nitrogen:

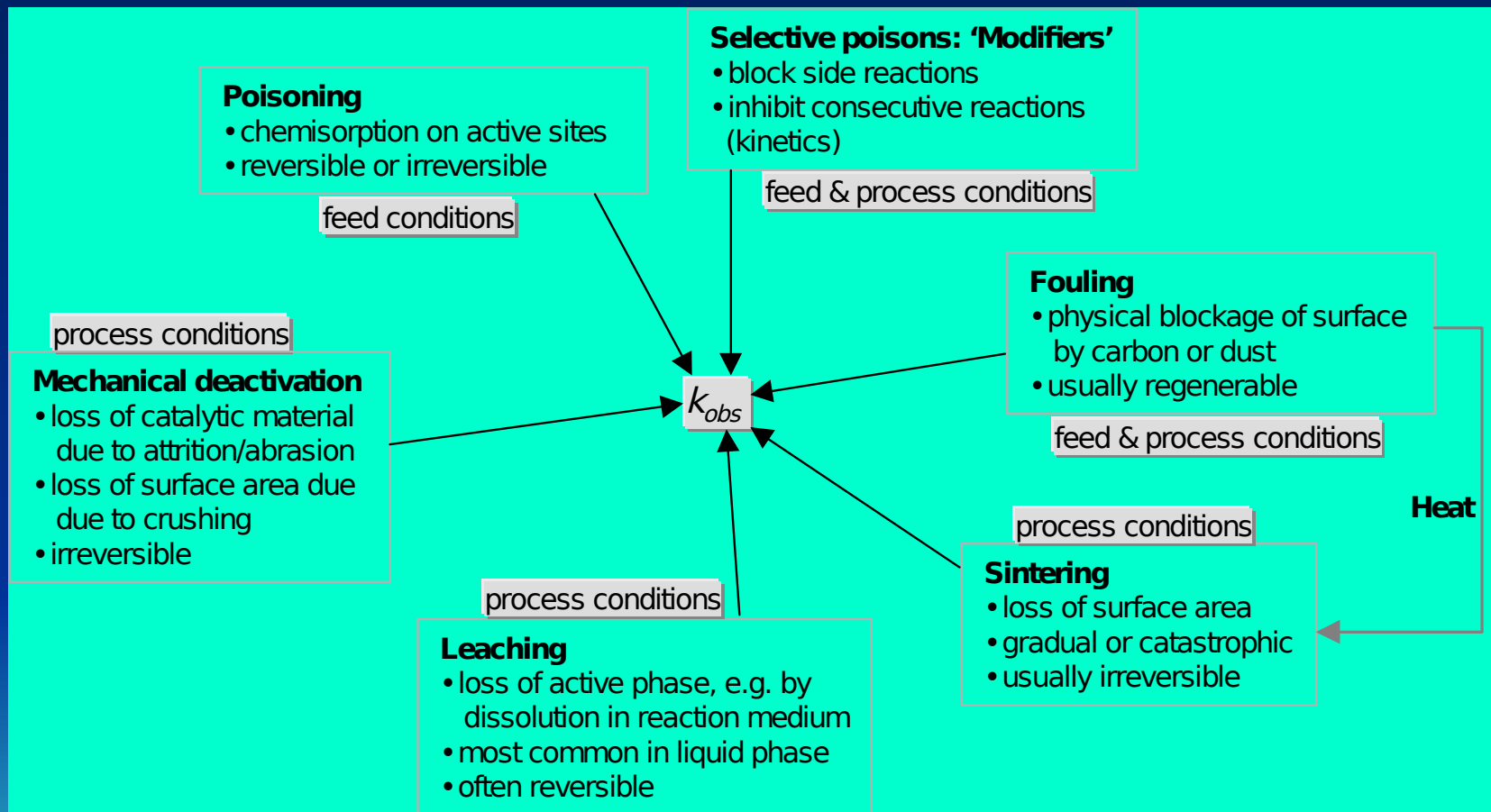
$$\rho = 0.808 \text{ g/cc at } -195.8^\circ\text{C}$$

$$\alpha = 16.2 \times 10^{-16} \text{ cm}^2 = 16.2 (\text{\AA}^0)^2$$

$$S = 4.35 \times 10^4 v_m \quad v_m \text{ is in CC at STP}$$

$$\text{Specific Surface area} = S/W \text{ cm}^2/\text{gm}$$

Deactivation - depends on?



FINISH

Physical Adsorption

- Texture and morphology
 - pore size
 - pore shape
 - pore-size distribution (same size or various sizes?)
 - pore volume
 - specific surface area of catalyst

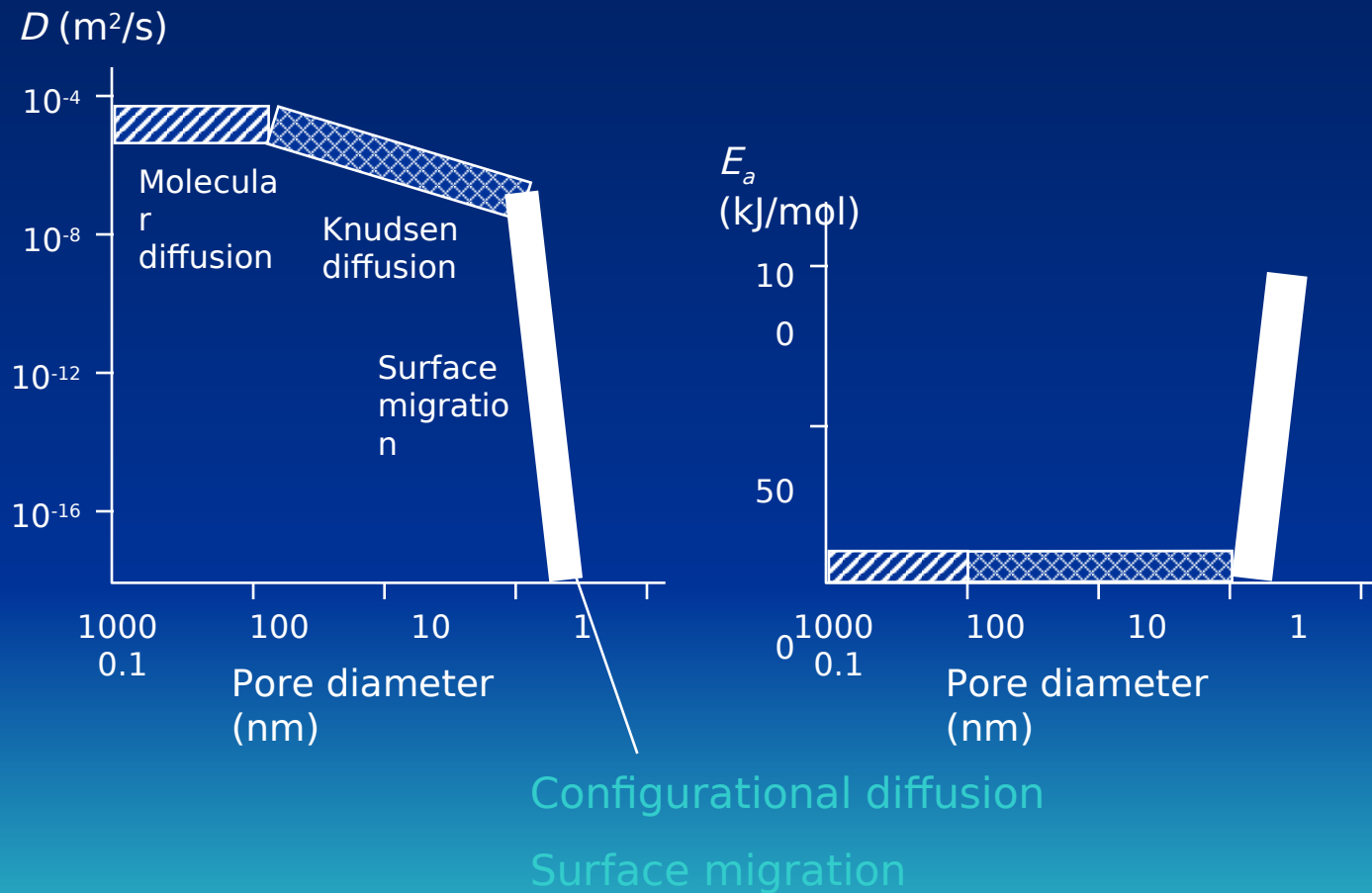
Internal Diffusion

- Types of diffusion
 - Molecular
 - Knudsen
 - Surface (also called “configurational diffusion”)
- Knudsen number: $K_n = \lambda/l$
 - λ = molecular free path length
 - l = characteristic pore diameter
 - $K_n \ll 1$ bulk diffusion
 - $K_n \gg 1$ Knudsen diffusion

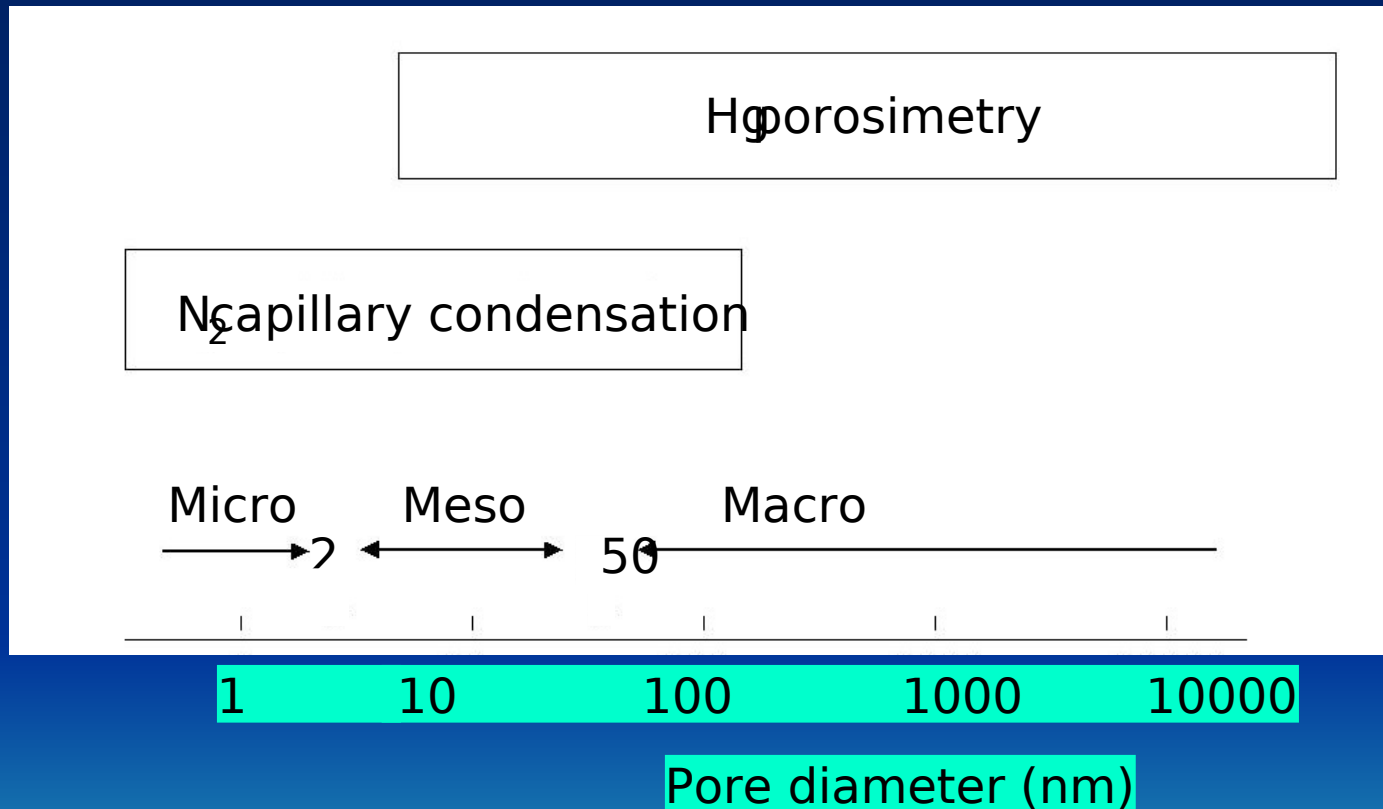
Pore Diameters, Shapes??

- Pore diameters
 - micropores (< 2 nm)
 - mesopores (2 - 50 nm)
 - macropores (> 50 nm)
- Experimental techniques
 - capillary condensation
 - Hg intrusion
 - microscopy
- Shapes
 - cylinder, slit, ink-bottle, wedge, ...

Pore Size and Diffusion Regimes

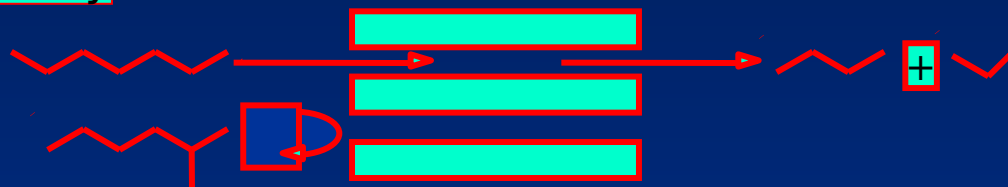


Pore Diameters and Measurement Techniques

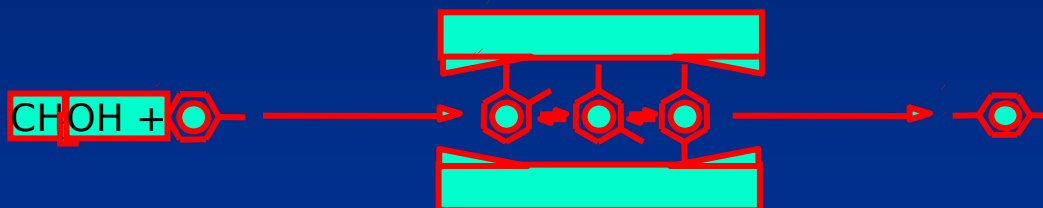


Shape Selectivity

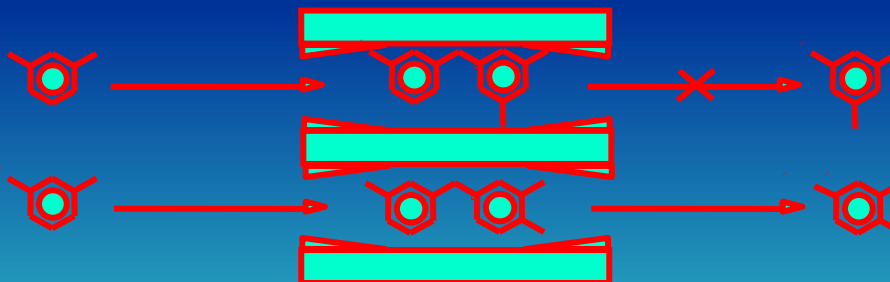
Reactant selectivity



Product selectivity



Restricted transition-state selectivity



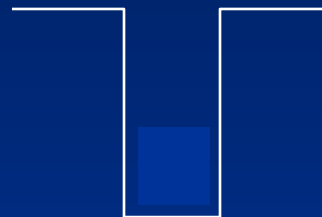
Pore Shapes

Slit



a

Cylindrical



b

Ink-bottle



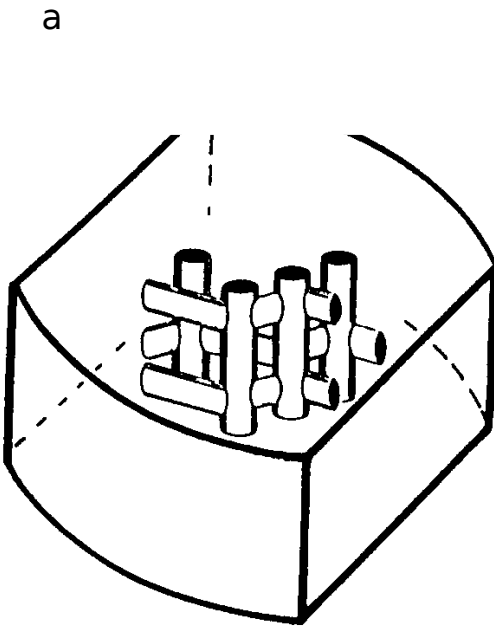
c

Wedge

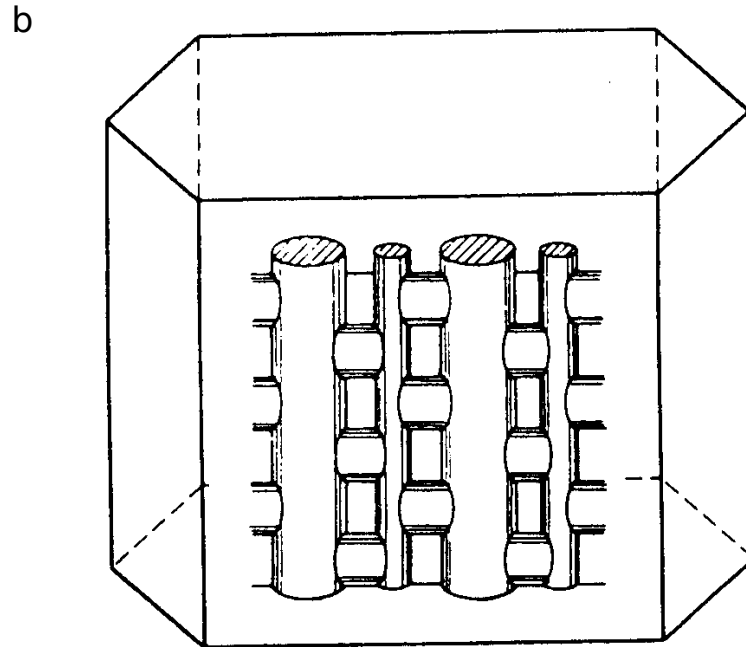


d

Pore Structures of Zeolites

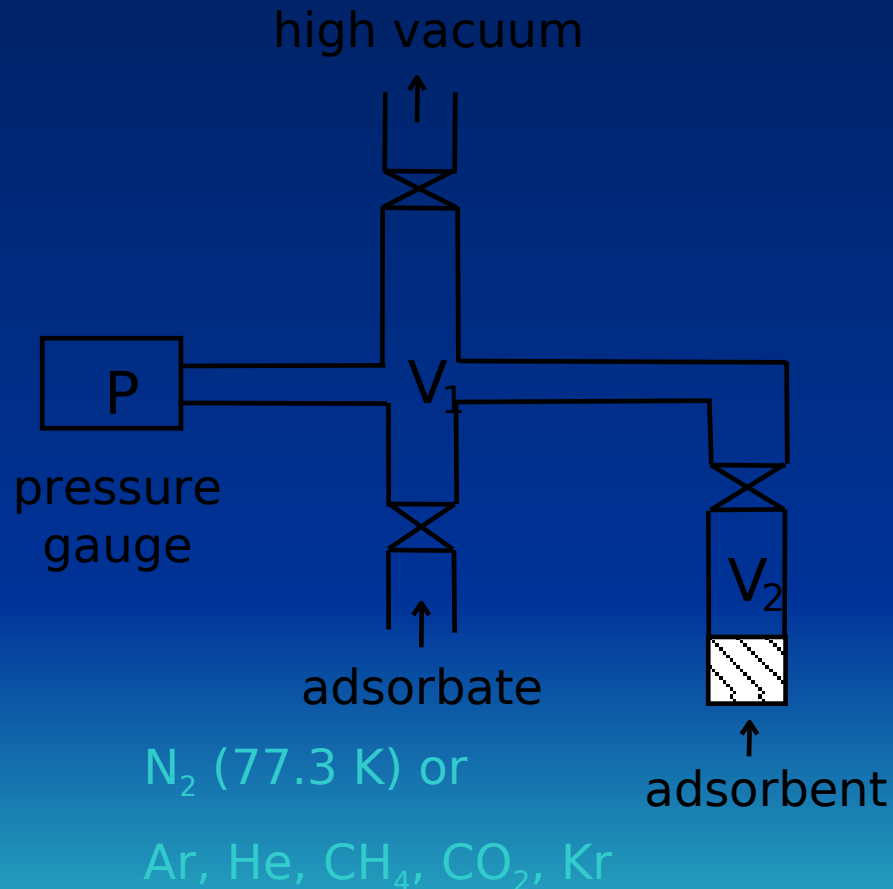


ZSM-5

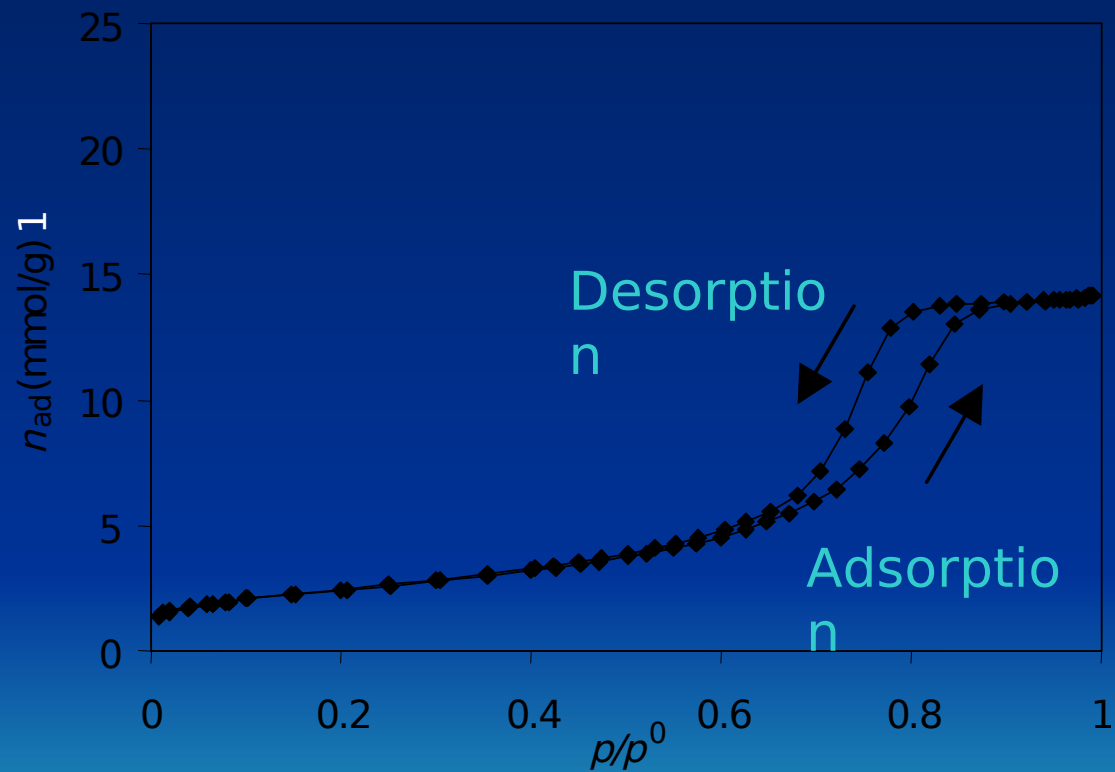


Mordenite

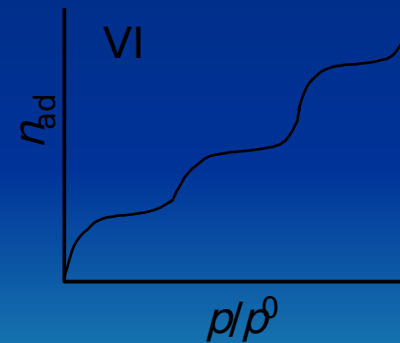
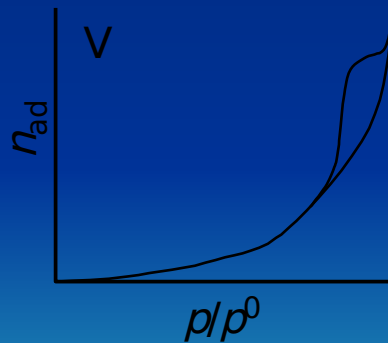
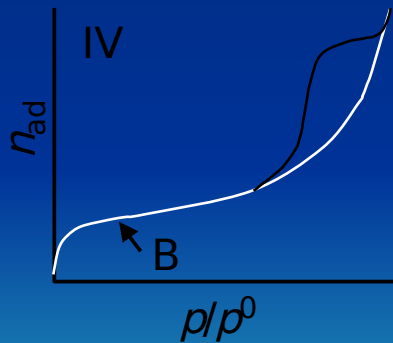
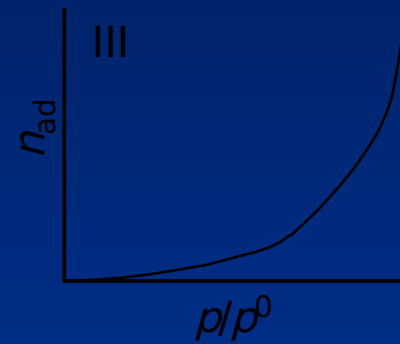
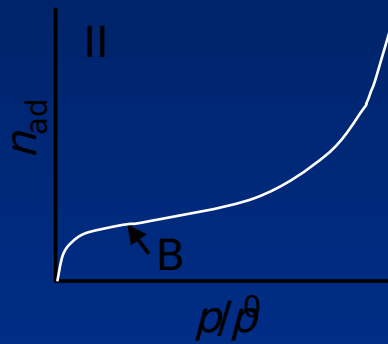
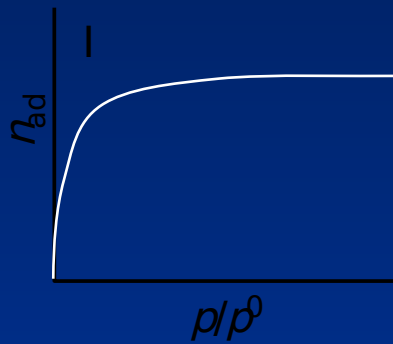
Volumetric Adsorption Measurement



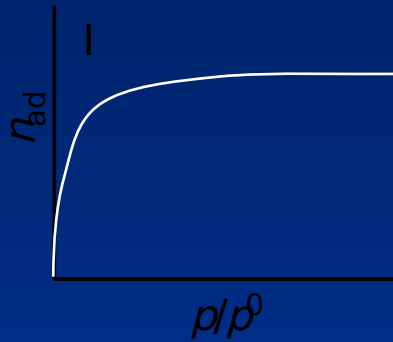
Adsorption Isotherms



Adsorption Isotherms



Langmuir Adsorption Isotherm (Type I)

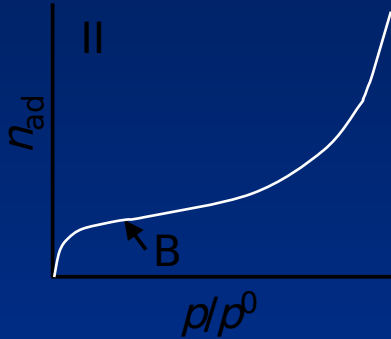


$$n_{ad} = n_m \cdot \theta = n_m \cdot \frac{K p}{1 + K p}$$

Assumptions:

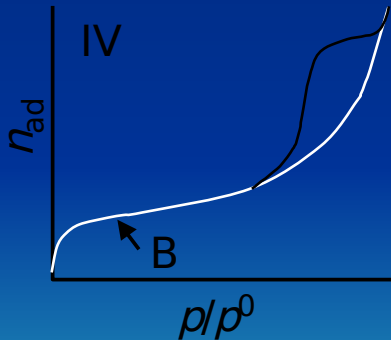
- homogeneous surface
(all adsorption sites energetically identical)
- monolayer adsorption (so no multilayer adsorption)
- no interaction between adsorbed molecules

Type II and IV Isotherms



Multilayer adsorption (starting at B)

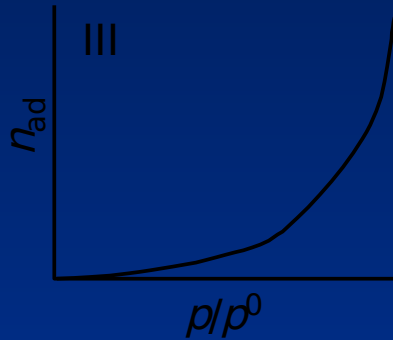
Common for pore-free materials



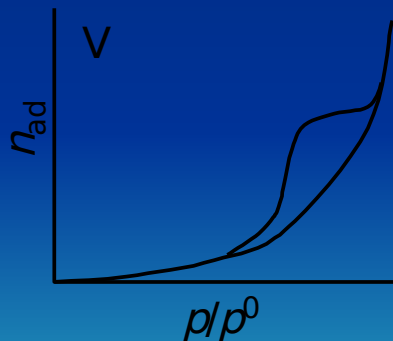
Similar to II at low p

Pore condensation at high p

Type III and V Isotherms



Strong cohesion force between adsorbed molecules, e.g. when water adsorbs on hydrophobic activated carbon



Similar to III at low p
Pore condensation at high p

Surface Area & Monolayer Capacity

specific surface
area (m^2/g)

Avogadro's number
(molecules/mol)

$$S = n_m A_m N_A$$

monolayer
capacity (mol/g)

area occupied by one
molecule
($\text{m}^2/\text{molecule}$)

BET model:

S_{BET}

t model:

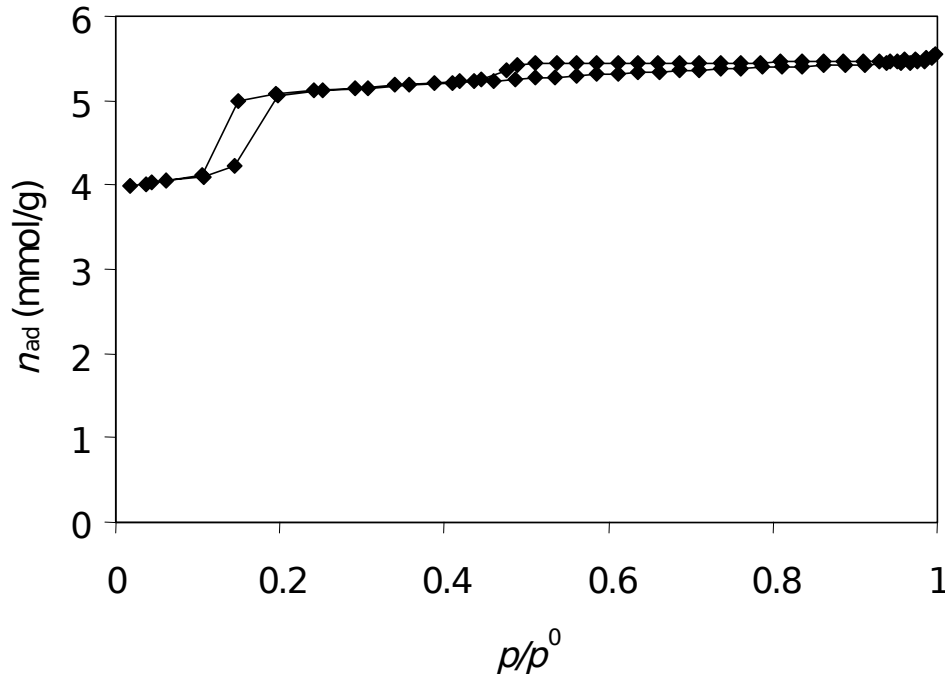
S_t

Properties of Adsorbates for Physisorption Measurements

Adsorbate	Boiling Point (K)	A_m (nm ² /molecule)
N ₂	77.3	0.162
Ar	87.4	0.142
CO ₂	194.5	0.17
Kr	120.8	0.152

N₂ Adsorption Isotherm in ZSM-5

Langmuir Adsorption?



No:

strong adsorption at low p
due to condensation in
micropores

at higher p saturation due to
finite (micro)pore volume

BET (Brunauer, Emmett, Teller) Method

- Modification of Langmuir isotherm
- Both monolayer and multilayer adsorption
- Layers of adsorbed molecules divided in:
 - First layer with heat of adsorption $\Delta H_{ad,1}$
 - Second and subsequent layers with $H_{ad,2} = \Delta H_{cond}$

BET isotherm:
$$\frac{p}{n_{ad}(p^0 - p)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \cdot \frac{p}{p^0}$$

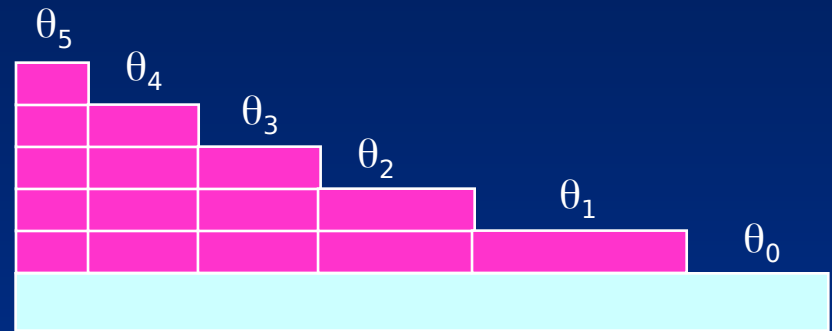
$$C = \exp\left(\frac{\Delta H_{ad} - \Delta H_{cond}}{RT}\right)$$

- BET equation does not fit entire adsorption isotherm
 - different mechanisms play a role at low and at high p

BET Model

reality

model



$$\sum \theta_i = 1 \quad n_{\text{ad}} = n_m (\theta_0 + 2\theta_1 + 3\theta_2 + \dots)$$

For every layer
Langmuir model

1st layer

$$k_a^0 \theta_0 p = k_d^1 \theta_1$$

$$\theta_1 = \frac{k_a^0}{k_d^1} p \theta_0 = K_1 p \theta_0$$

nth layer

$$k_a^{n-1} \theta_{n-1} p = k_d^n \theta_n$$

$$\theta_n = \frac{k_a^{n-1}}{k_d^n} p \theta_{n-1} = K_n p \theta_{n-1}$$

Assume

$$K_1 = K_{1,0} e^{-\frac{\Delta H_{\text{ads}}}{RT}}$$

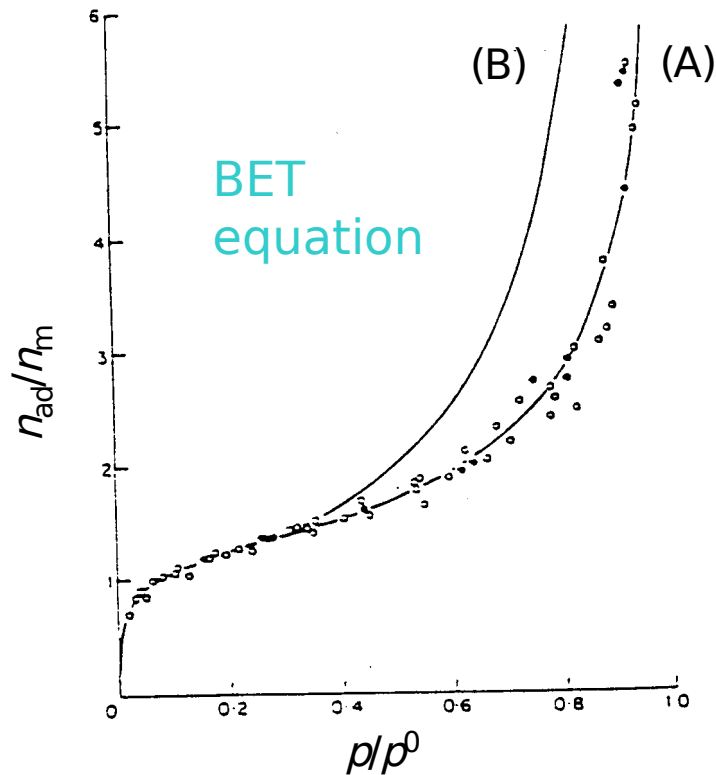
$$K_n = K_{n,0} e^{-\frac{\Delta H_n}{RT}} \approx K_{n,0} e^{-\frac{\Delta H_{\text{cond}}}{RT}}$$



$$\frac{n_{\text{ad}}}{n_m} = \frac{C}{\left(1 - \frac{p}{p^0}\right) \left(1 + (C-1) \frac{p}{p^0}\right)}$$

with $C = e^{\frac{\Delta H_{\text{ads}} - \Delta H_{\text{cond}}}{RT}}$

Non-Porous Silica and Alumina



Low p/p_0 :

- filling of micropores
- favoured adsorption at most reactive sites (heterogeneity)

High p/p_0 :

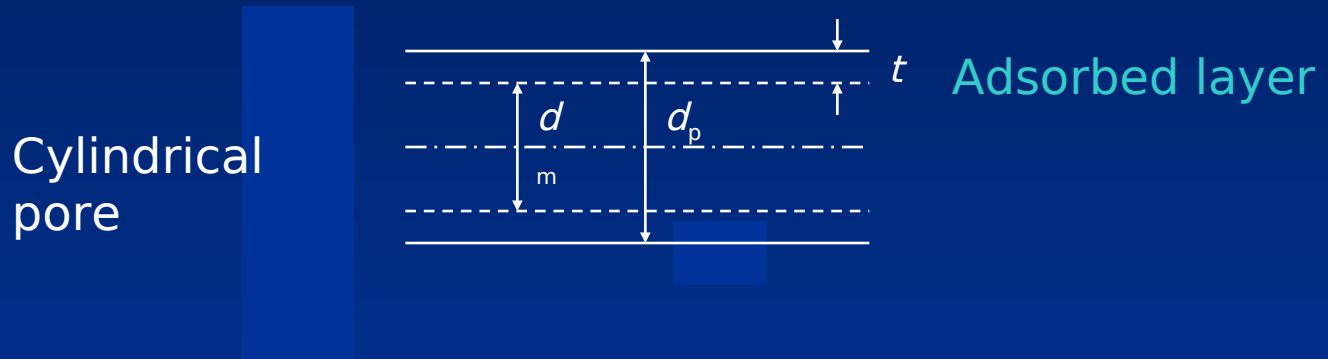
- capillary condensation

Range $0.05 < p/p_0 < 0.3$
is used to determine S_{BET}

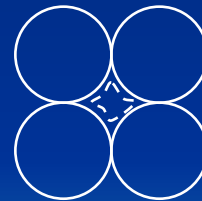
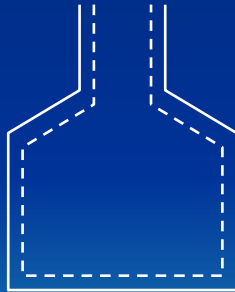
Texture Data of Commercial Catalysts

Material	Mean d_p (nm)	S_{BET} (m ² /g)
Catalyst supports		
Silica gel	10	200
	6	400
	4	800
γ -Al ₂ O ₃	10	150
	5	500
Zeolite	0.6-2	400-800
Activated carbon	2	700-1200
TiO ₂	400-800	2-50
Aerosil SiO ₂	-	50-200
Catalysts		
MeOH synthesis (Cu/ZnO/Al ₂ O ₃)	20	80
NH ₃ synthesis (Fe/Al ₂ O ₃ /K ₂ O)	100	10
Reforming (Pt/Re/Al ₂ O ₃)	5	250
Epoxidation (Ag/ α -Al ₂ O ₃)	200	0.5

Adsorption at Pore Wall



Ink-bottle
pore



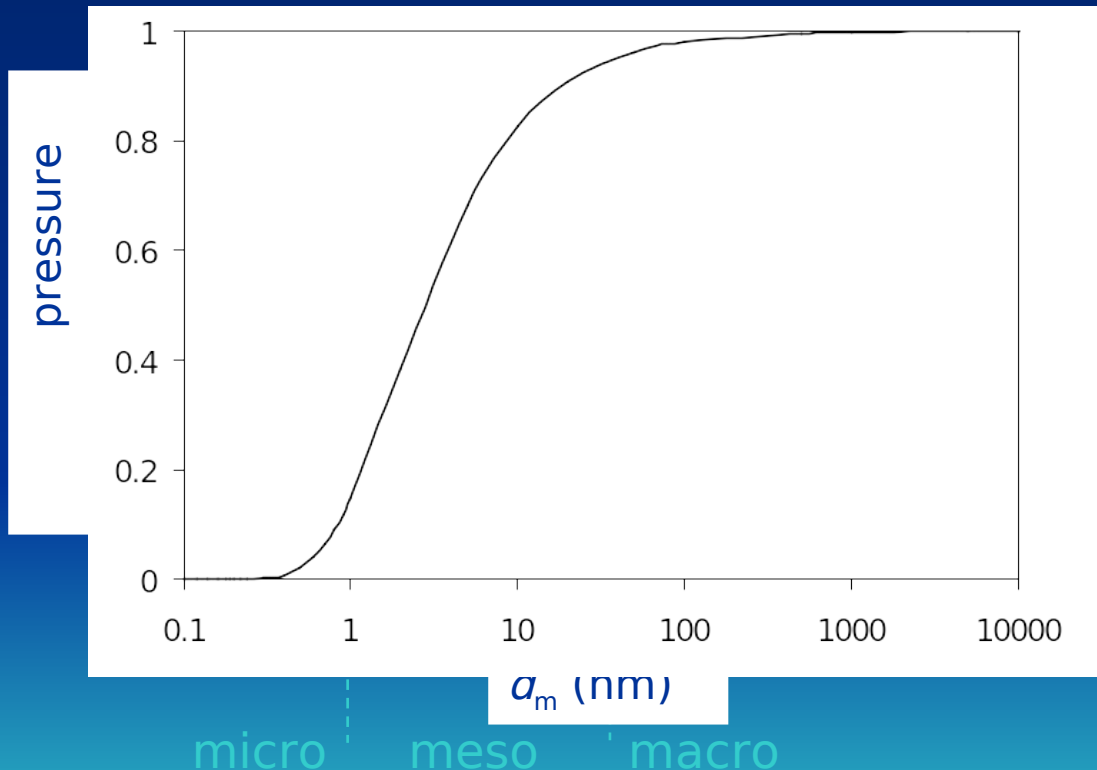
Pore with shape of interstice
between close-packed
particles

Kelvin Equation for Nitrogen

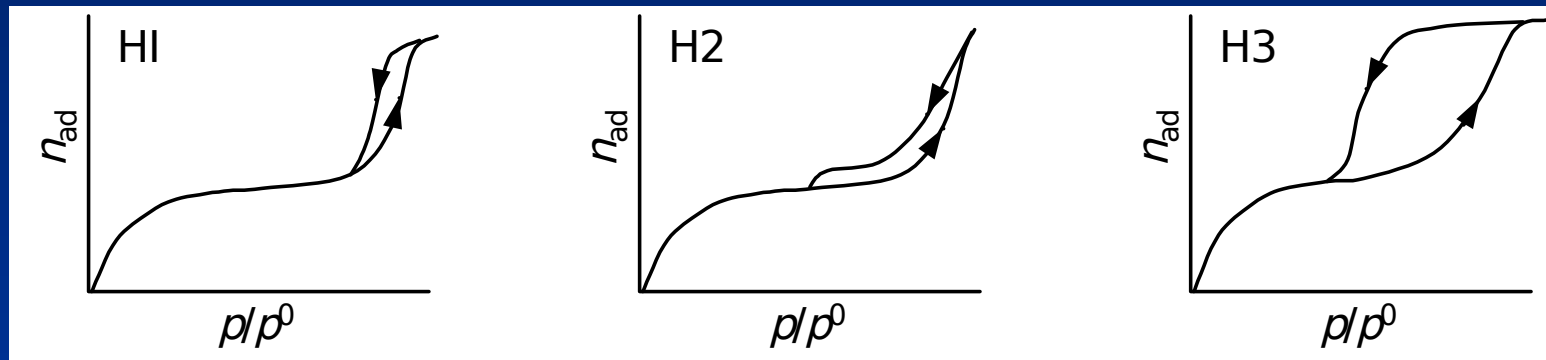
$$\ln \frac{p}{p^0} = - \frac{2\gamma V_L}{RT} \frac{1}{r_m}$$

$$V_L = 34.68 \cdot 10^{-6} \text{ m}^3/\text{mol}$$

$$\gamma = 8.88 \text{ mN/m}$$



Hysteresis Loops



Information on pore
shape

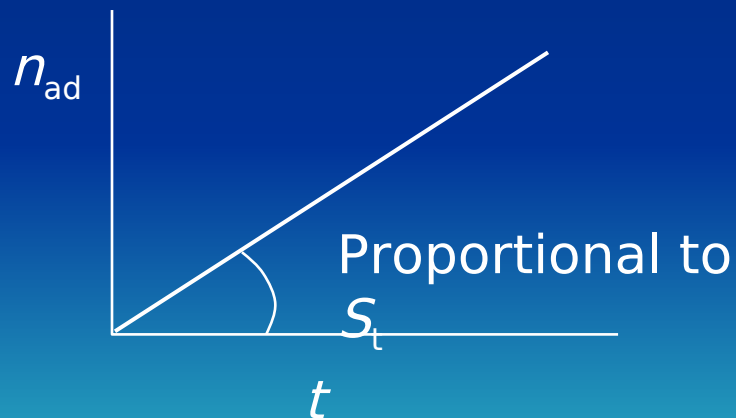
t -method

$$t = \frac{n_{\text{ad}}}{n_{\text{m}}} \cdot 0.354 \text{ nm}$$

$$S_{\text{t}} = n_{\text{m}} \cdot A_{\text{m}} \cdot N$$

$$\Rightarrow S_{\text{t}} = \frac{n_{\text{ad}}}{t} \cdot 0.354 \cdot 10^{-9} \cdot A_{\text{m}} \cdot N$$

$$\Rightarrow S_{\text{t}} = 5.73 \cdot 10^{-6} \cdot \frac{n_{\text{ad}}}{t}$$



Note:

n_{ad} is experimental result

t is calculated from correlation t versus p

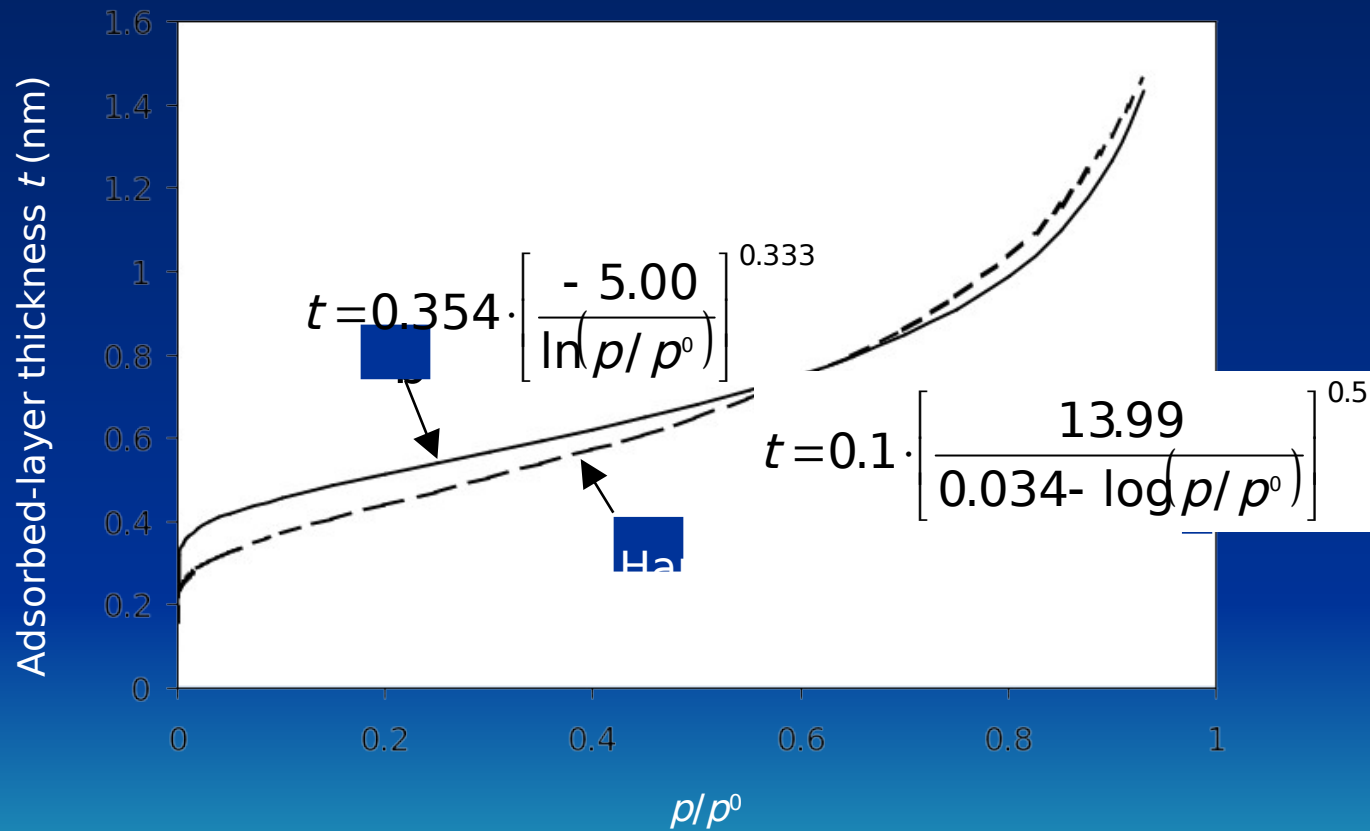
t -method

- BET
 - only valid in small pressure interval
 - interpretation not very easy
- thickness (t) of adsorbed layer can be calculated

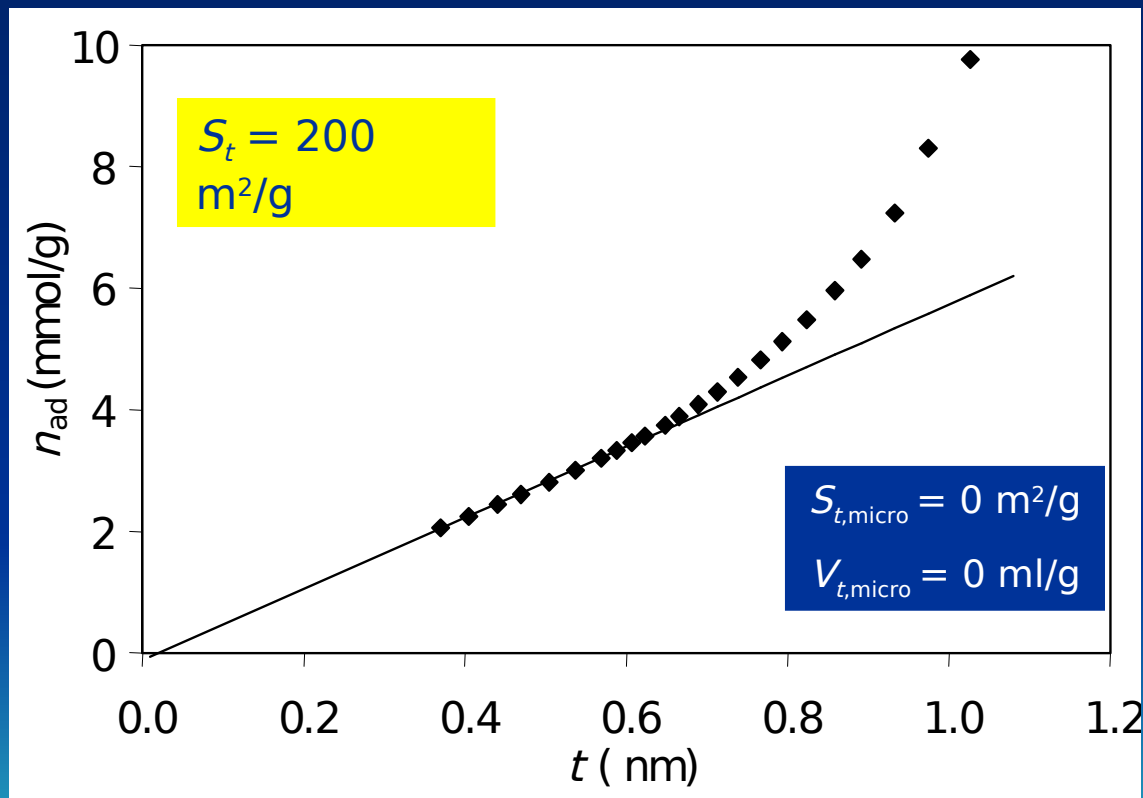


- plot of t versus p for non-porous materials is the same (has been checked experimentally)
- t -plot helps in interpretation

t -curves



t -plot of γ -alumina



Shape of t -plots

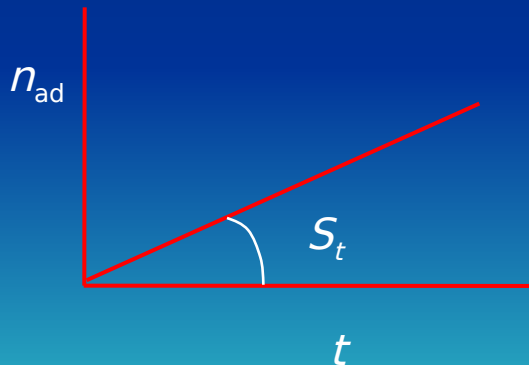
$$t = \frac{n_{\text{ad}}}{n_{\text{m}}} \cdot 0.354 \text{ nm}$$

Adsorption isotherm

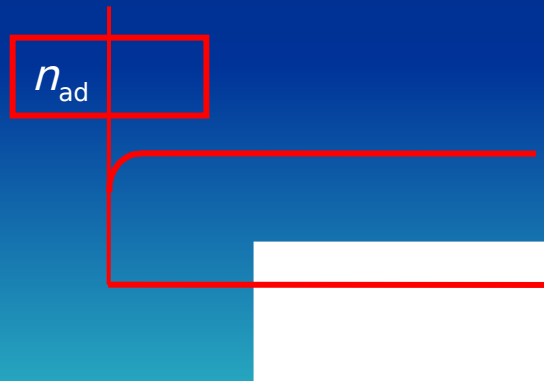


$$t = f(p) \downarrow$$

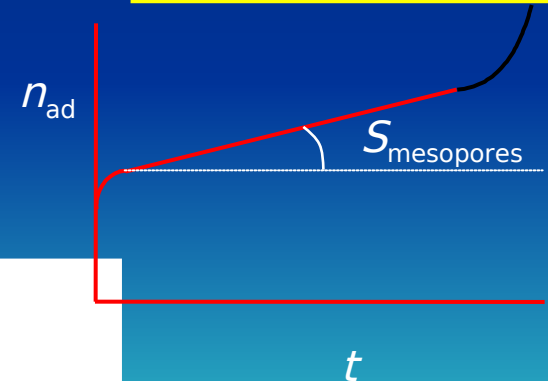
Non-porous



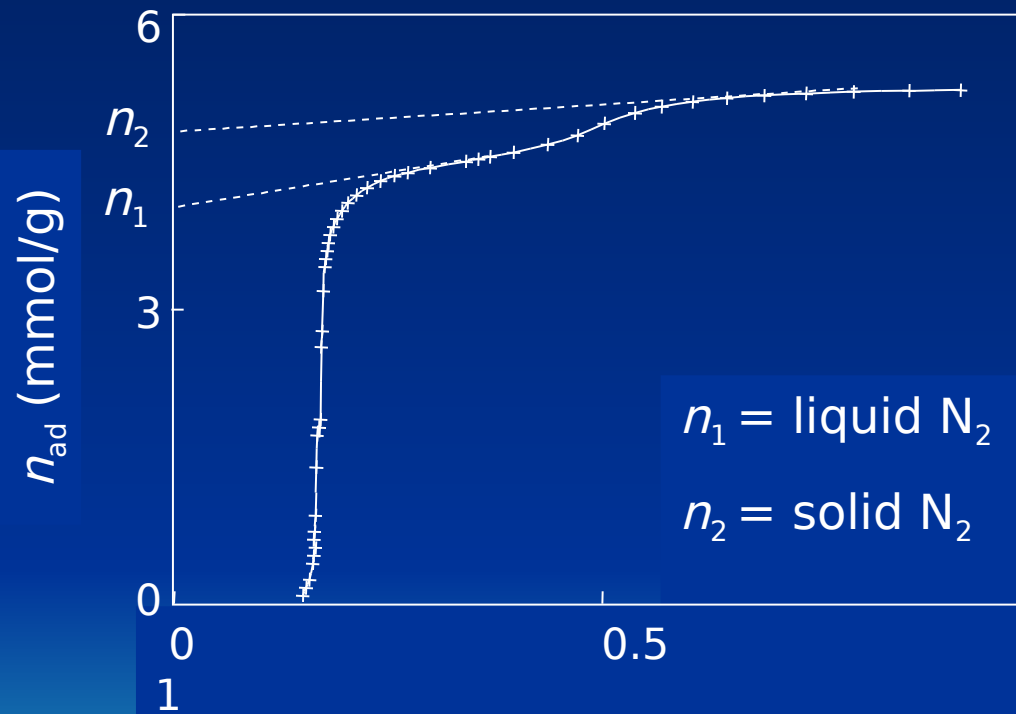
Microporous



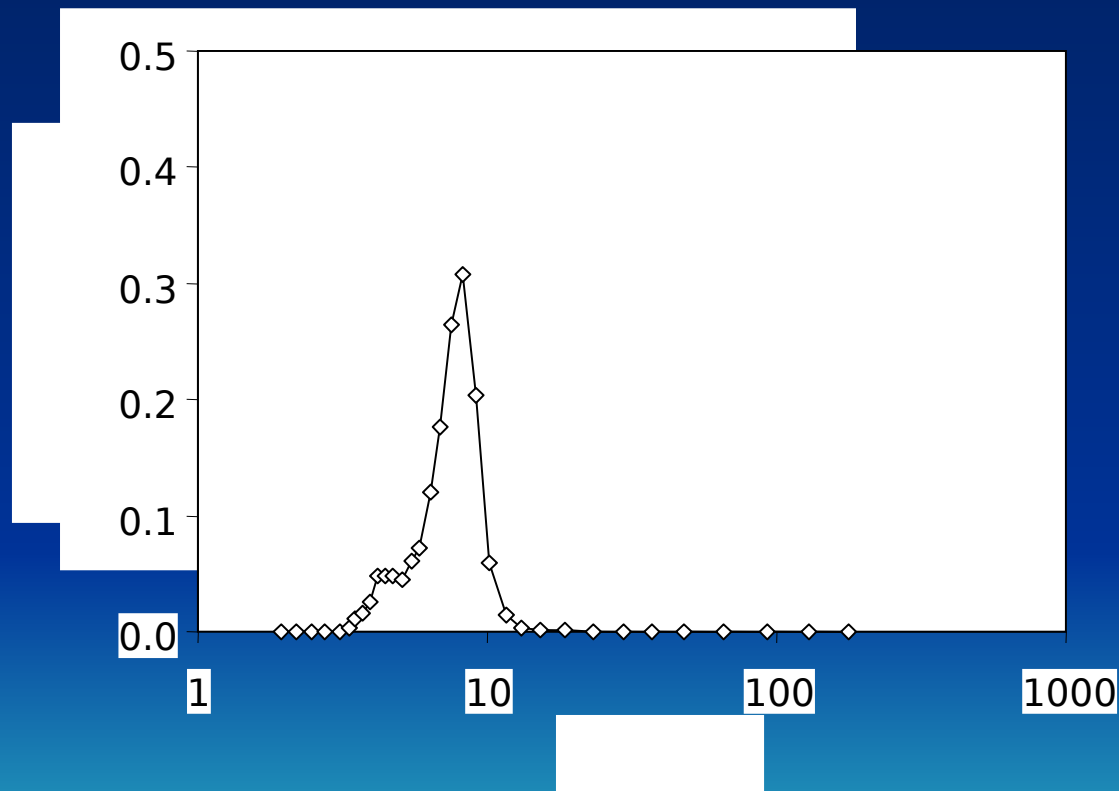
Micro- and mesoporous



t -plot of N₂ Physisorption on ZSM-5



Pore-Size Distribution of γ -Alumina



Mercury Intrusion Porosimetry

- Hg does not wet surfaces; pressure is needed to force intrusion

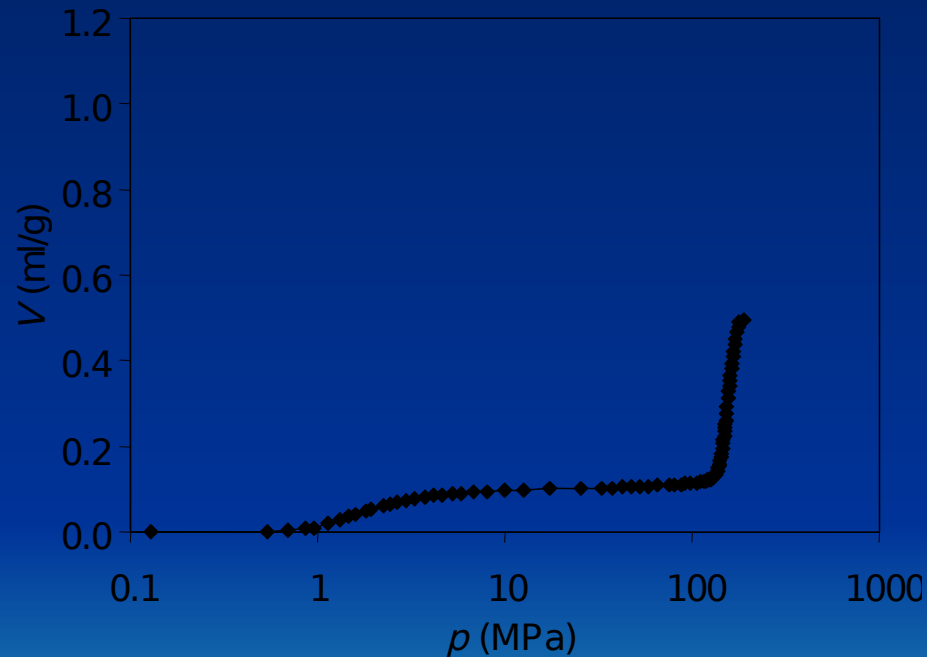
- From a force balance:

$$d_p = \frac{14860}{p}$$

(d in nm, p in bar)

- Convenient method for determining pore volume versus pore size

Mercury Intrusion Curve of γ -Alumina



Surface Area's - S_{Hg} and S_{BET}

Adsorbent	S_{Hg} m ² /g	S_{BET} m ² /g	θ deg
Iron Oxide	14.3	13.3	130
Tungsten Oxide	0.11	0.10	130
Anatase	15.1	10.3	130
Hydroxy Apatite	55.2	55.0	130
Carbon Black (Spheron-6)	107.8	110.0	130
0.5 % Ru/ γ -Al ₂ O ₃	237.0	229.0	140
0.5 % Pd/ γ -Al ₂ O ₃	115.0	112.0	140
TiO ₂ Powder	31.0	25.0	140
Sintered Silica Pellets	20.5	5.0	140
Zeolite H-ZSM-5	39.0	375.0	140
Norit Active Carbon R1 Extra	112.0	915.0	140

Discrepancy S_{Hg} and S_{BET} for Microporous Materials

- Hg cannot penetrate small (micro)pores, N_2 can
- Uncertainty of contact angle and surface tension values
- Cracking or deforming of samples

Texture Properties

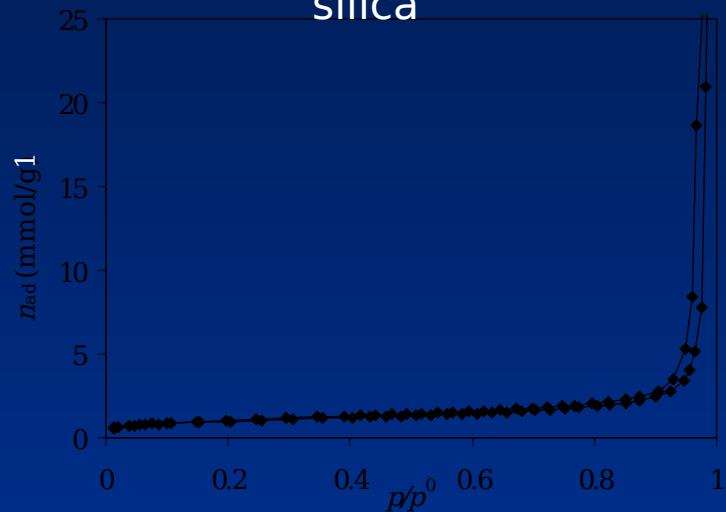
	N ₂ -physisorption				Hg-porosimetry		
	S_{BET}	S_t	V_p	d_p	S_{Hg}	V_p	d_p
	m ² /g	m ² /g	ml/g	nm	m ² /g	ml/g	nm
Wide Pore Silica	78	52	0.91	47	80	0.92	54
γ-Alumina	196	202	0.49	10	163	0.49	10
α-Alumina	9	8	0.12	112	12	0.48	150
Active Carbon	1057 ^a	28	0.51	2	0.6	0.46	106
Raney Ni	76	-	0.14	5.80	-	-	-
ZSM-5	345	344	0.19	0.58	11	1.1	820 ^b

^a p/p_0 range of 0.01-0.1 was used in the calculation.

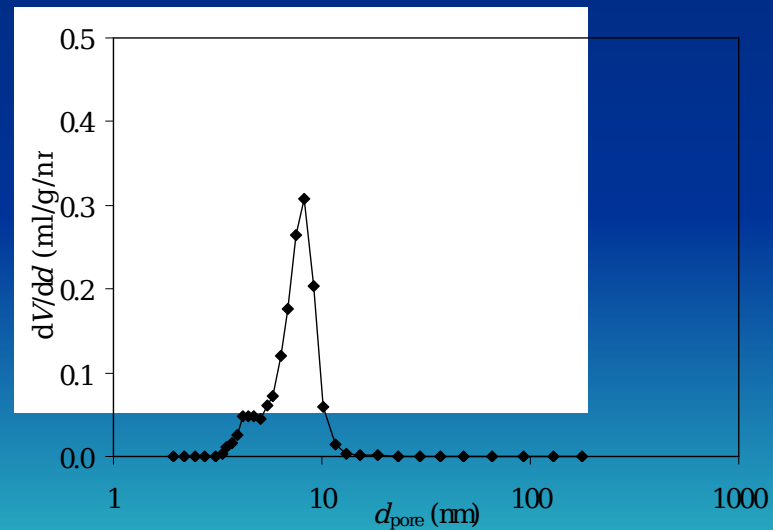
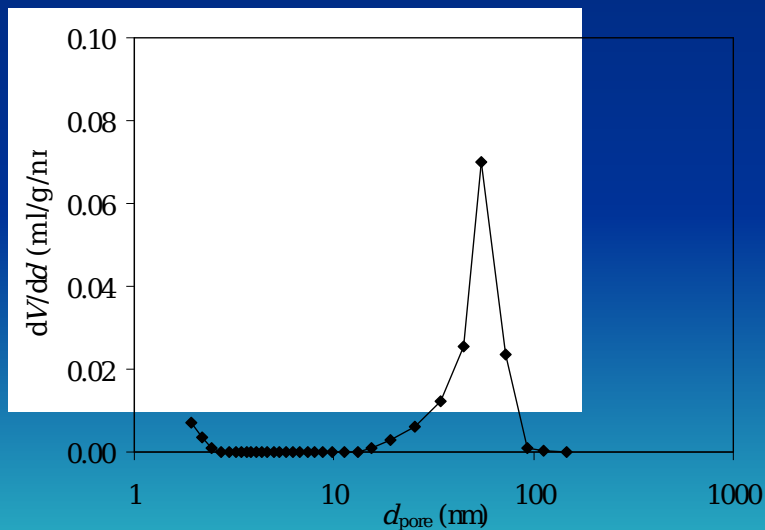
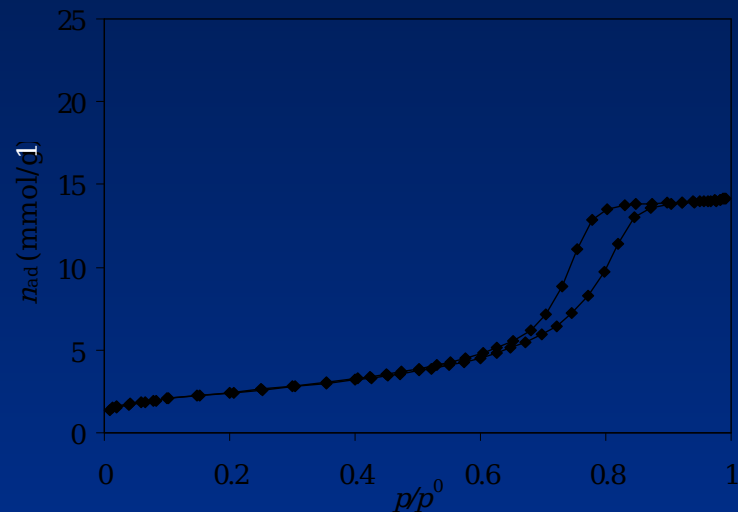
^b intraparticle voids.

N₂ Adsorption Isotherms & Pore Volume Distributions

wide-pore
silica

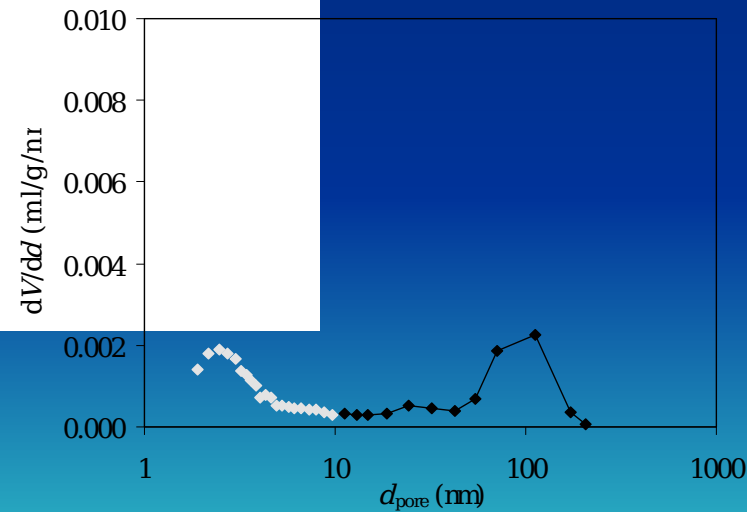
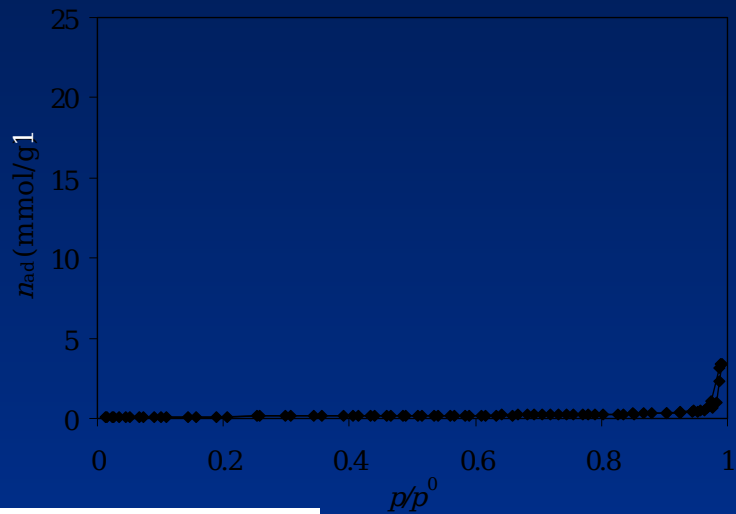


γ -alumina

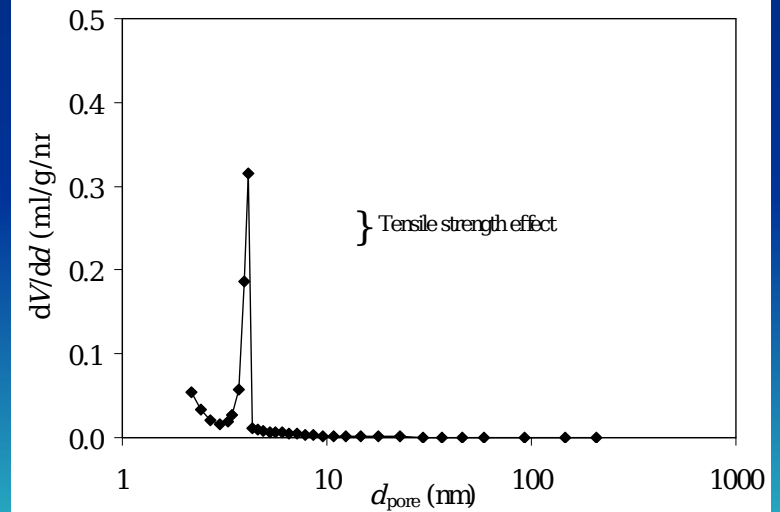
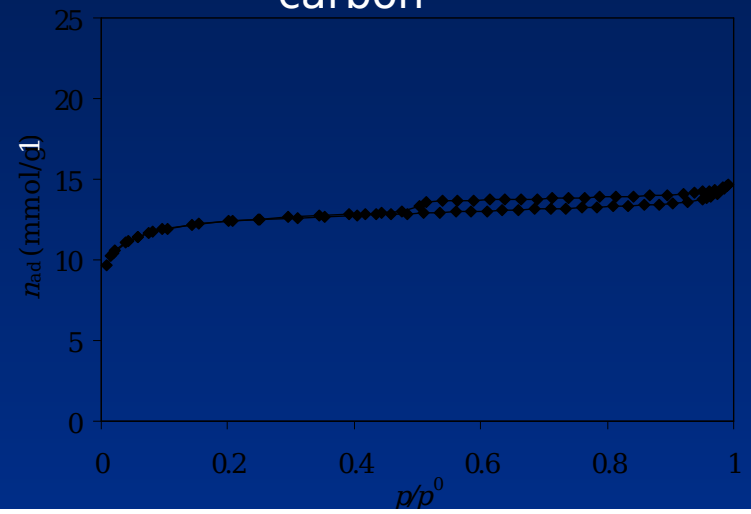


N₂ Adsorption Isotherms & Pore Volume Distributions

α -alumina



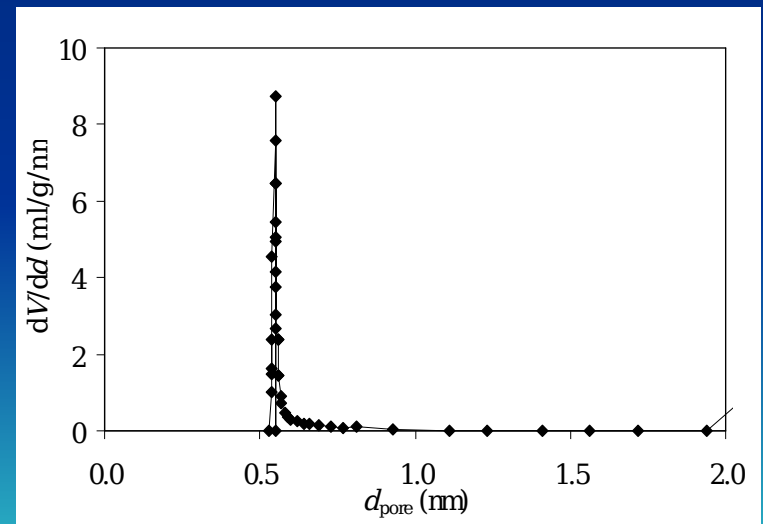
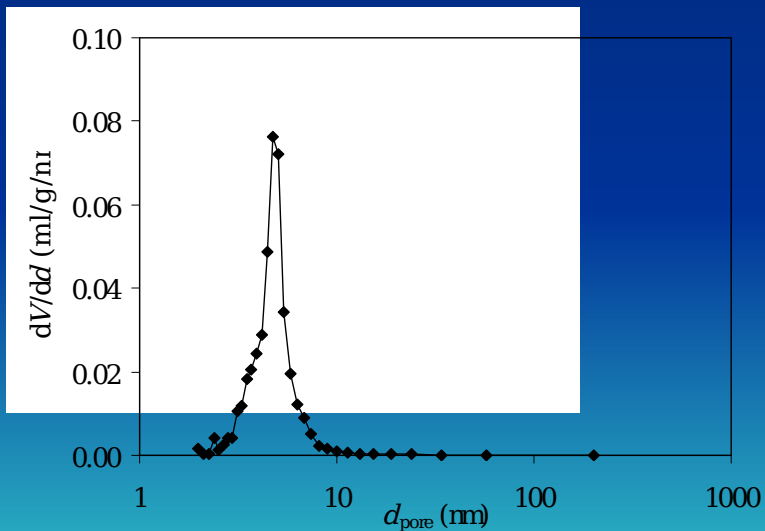
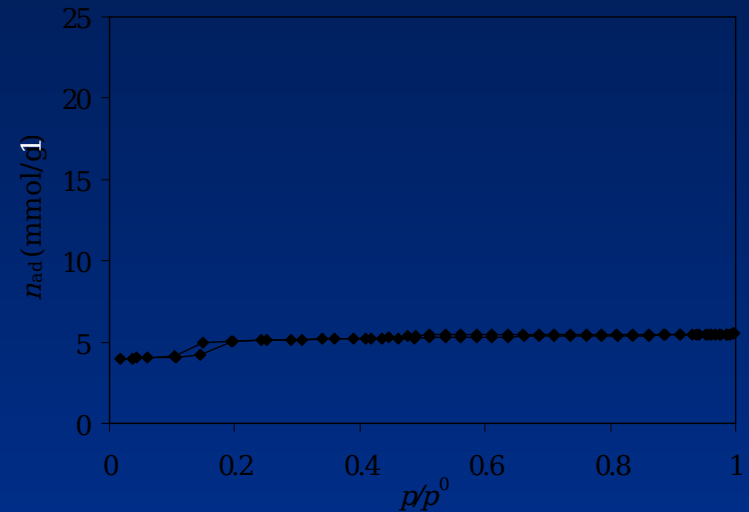
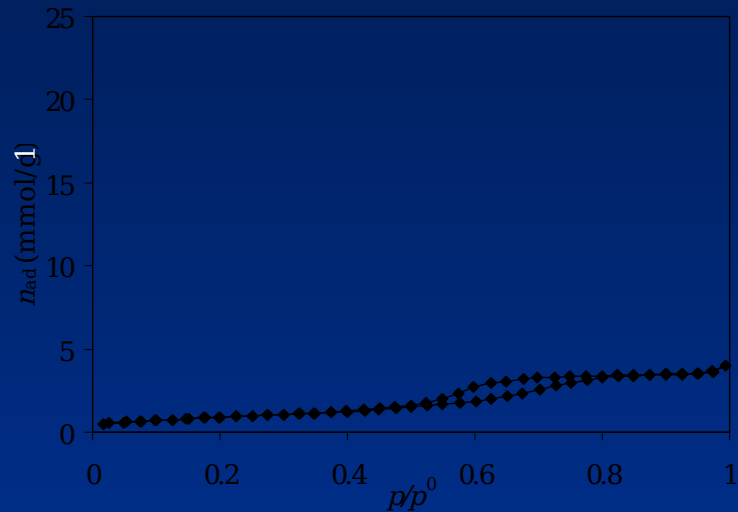
activated
carbon



N₂ Adsorption Isotherms & Pore Volume Distributions

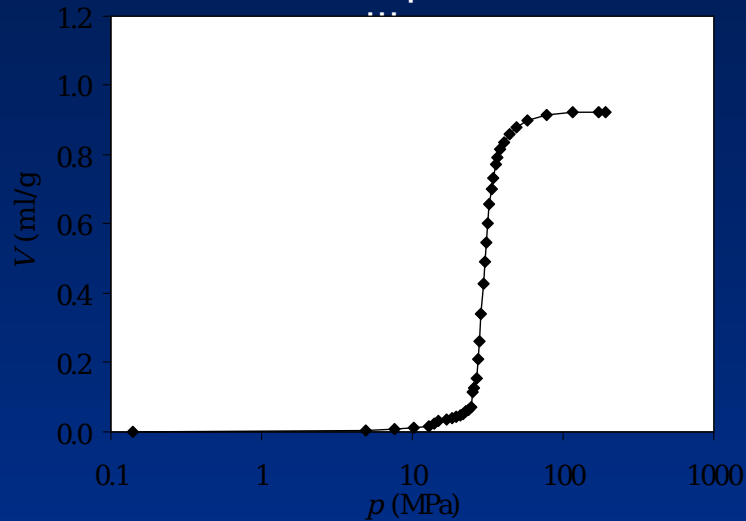
Raney Ni

ZSM-5

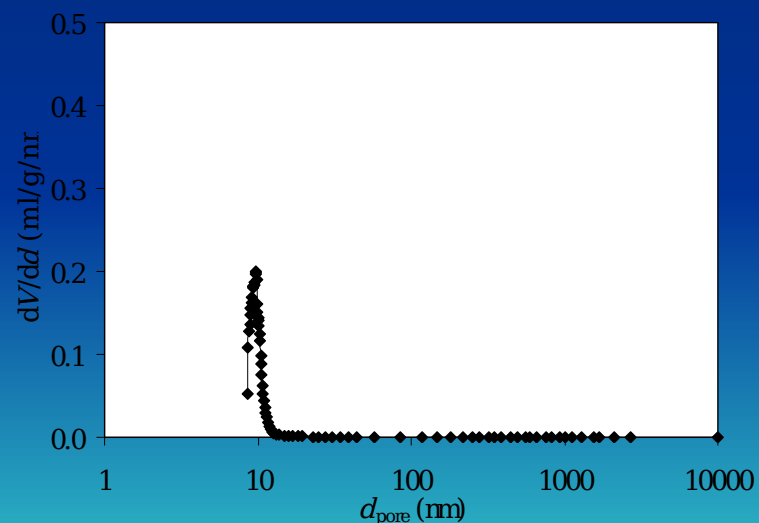
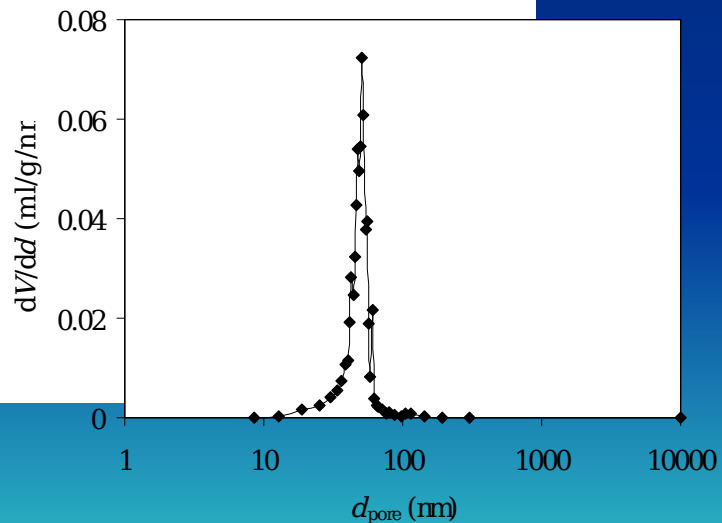
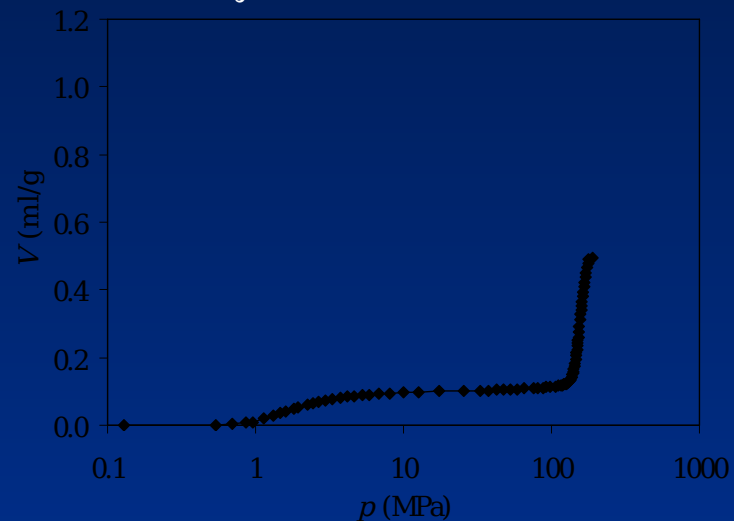


Hg Intrusion Curves & Pore Volume Distributions

wide-pore

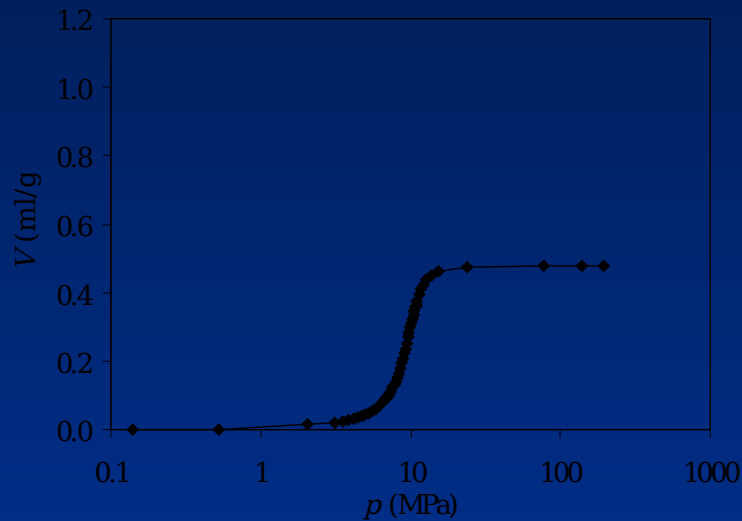


γ -alumina

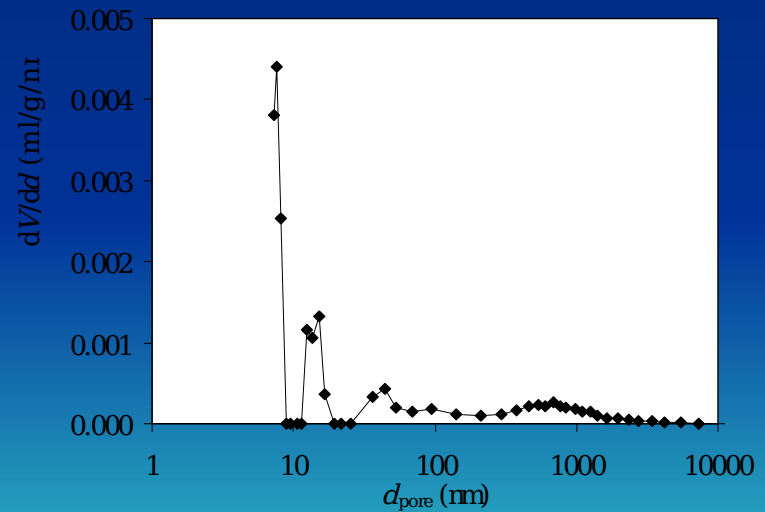
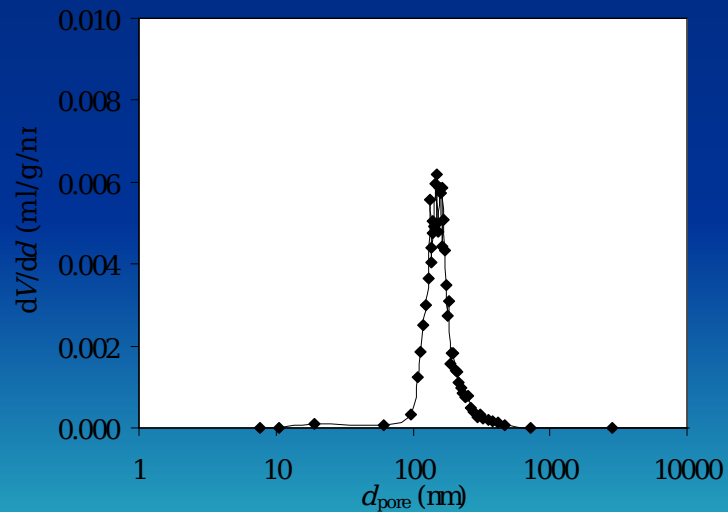
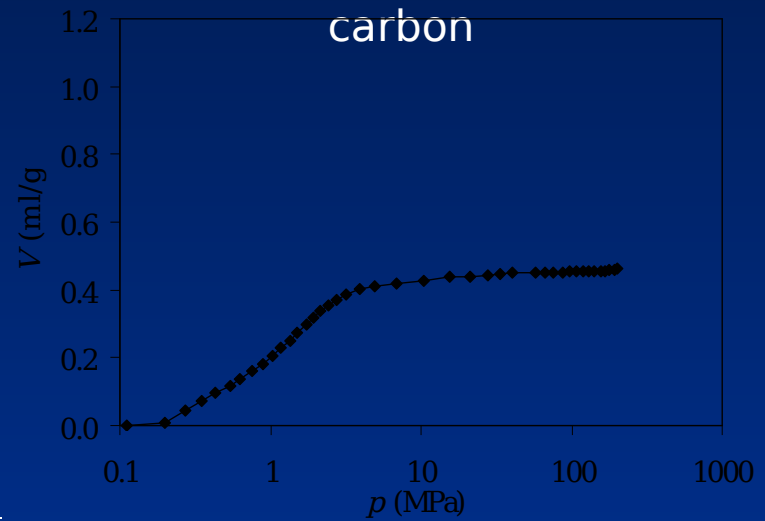


Hg Intrusion Curves & Pore Volume Distributions

α -alumina

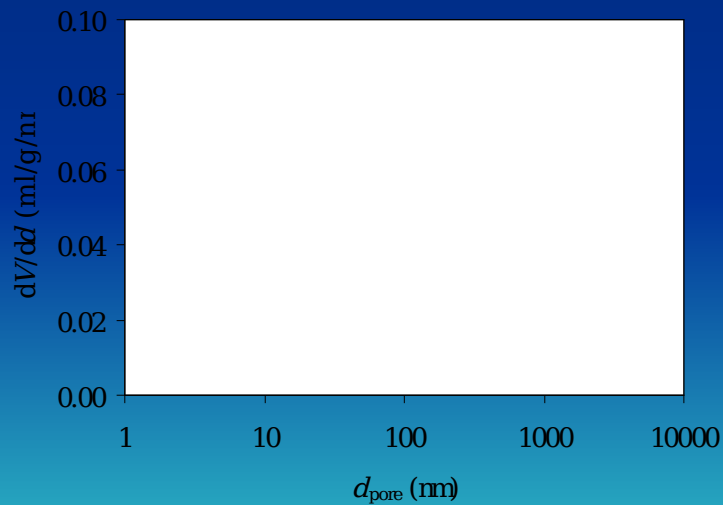
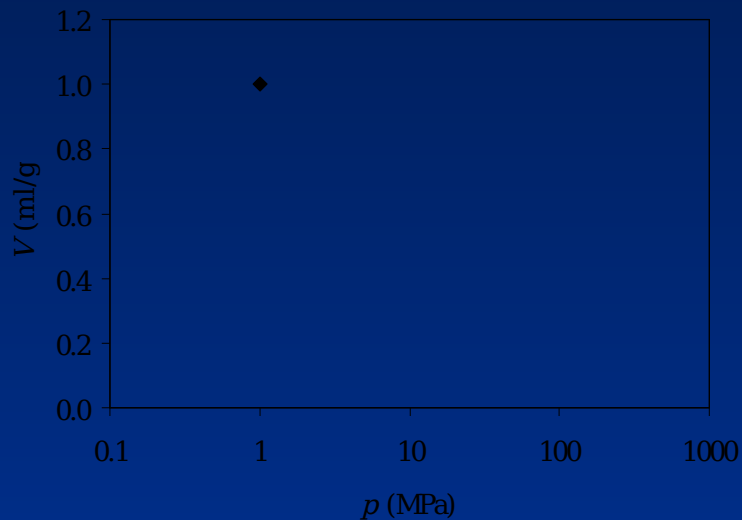


activated
carbon

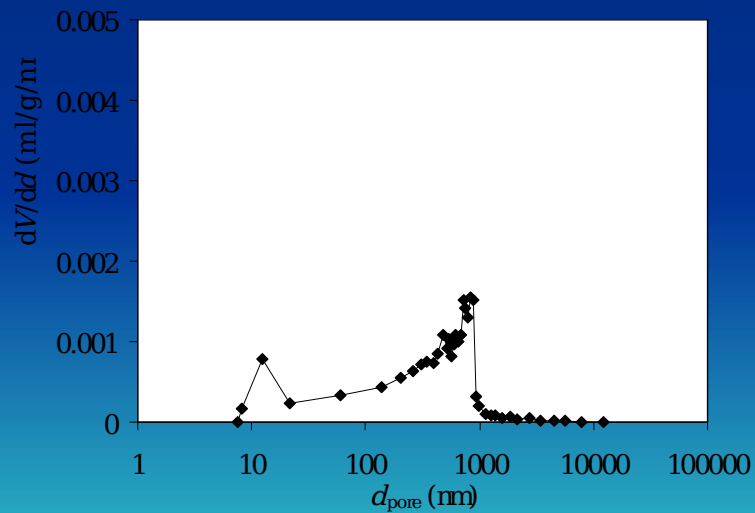
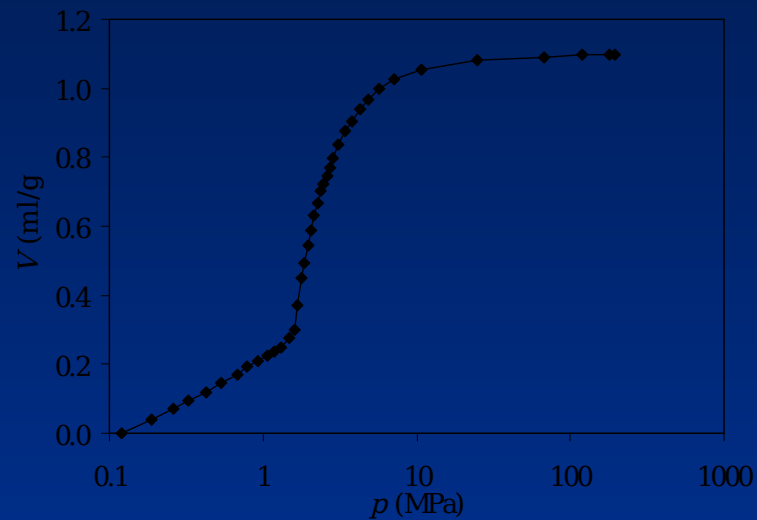


Hg Intrusion Curves & Pore Volume Distributions

Raney Ni

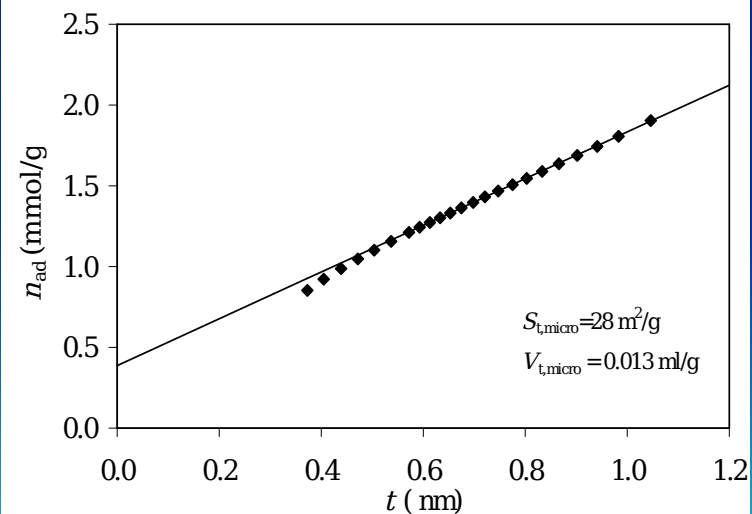
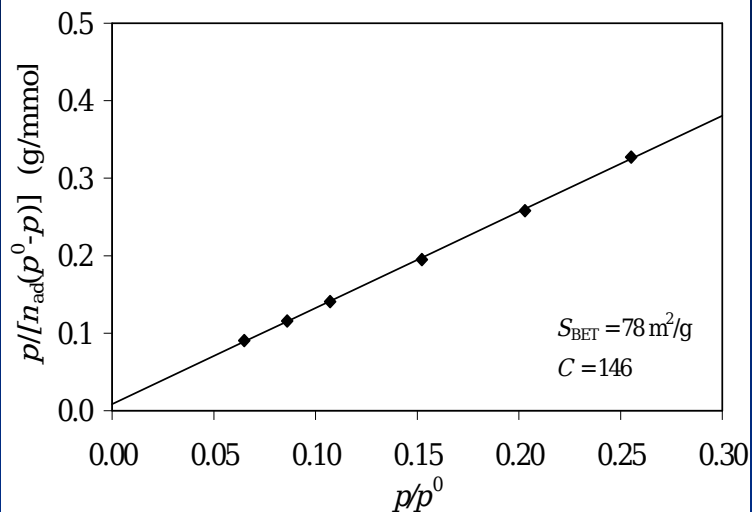


ZSM-5

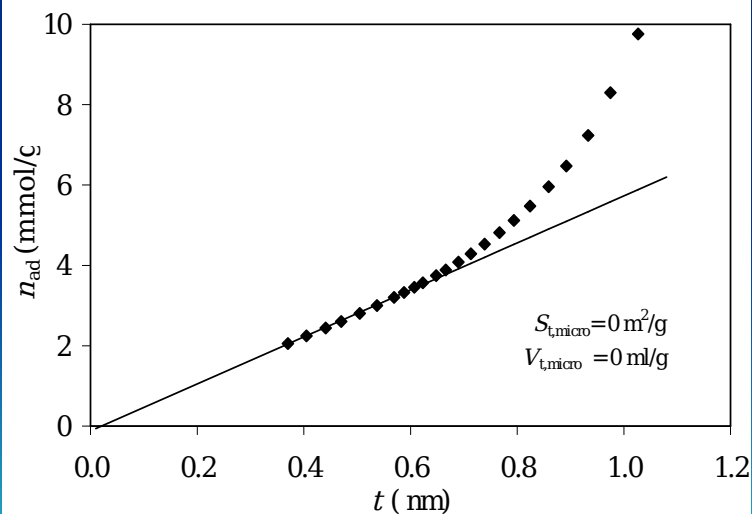
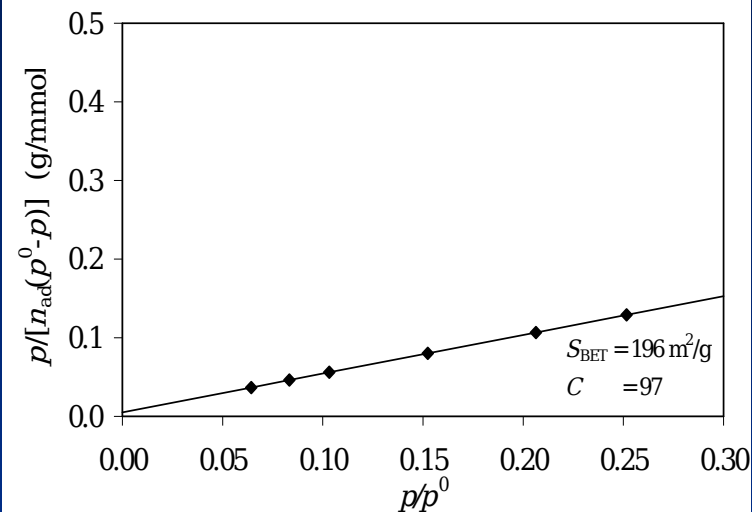


BET- & *t*-plots

wide-pore

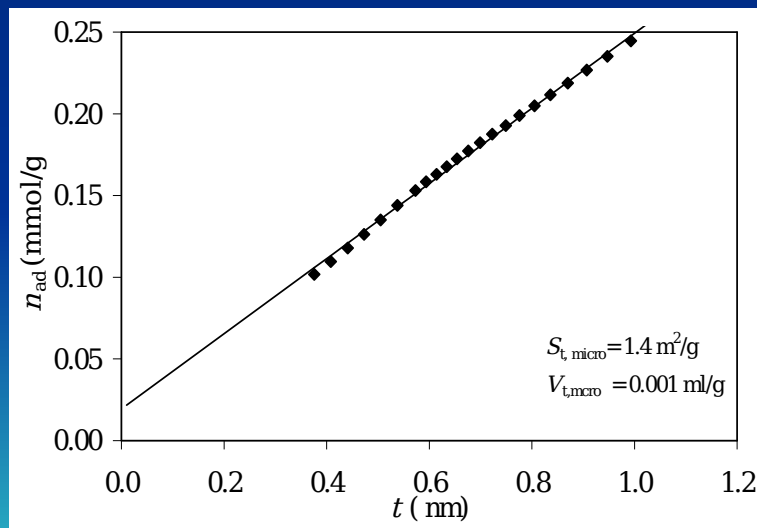
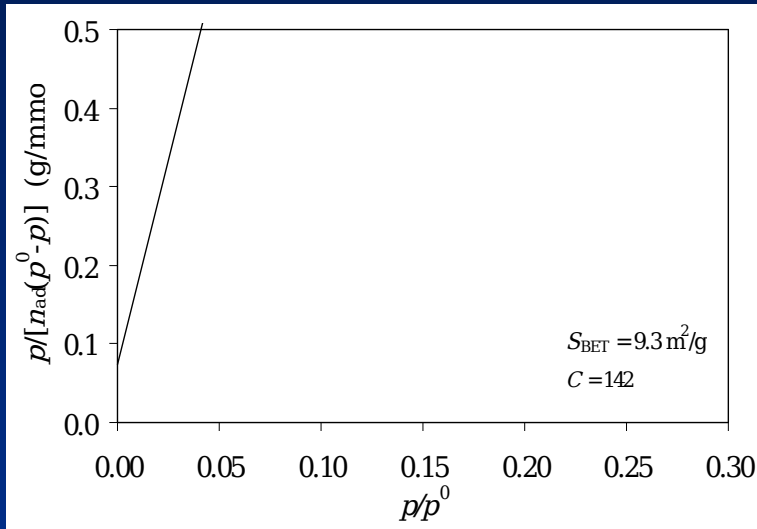


γ -alumina

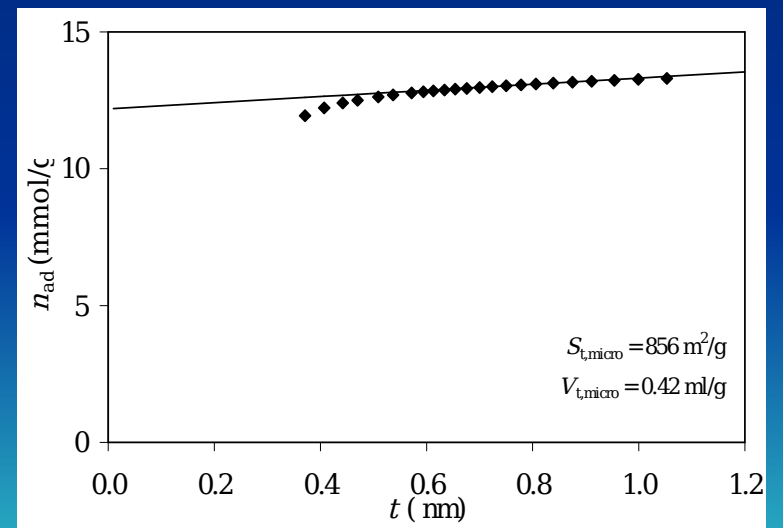
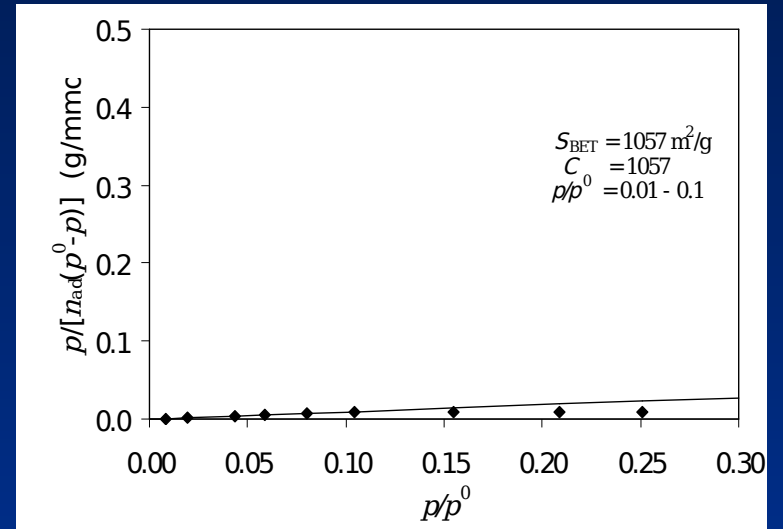


BET- & t -plots

α -alumina

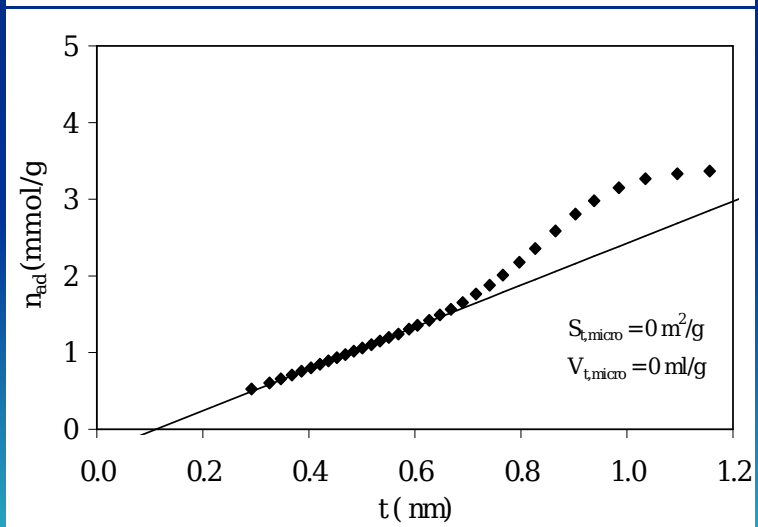
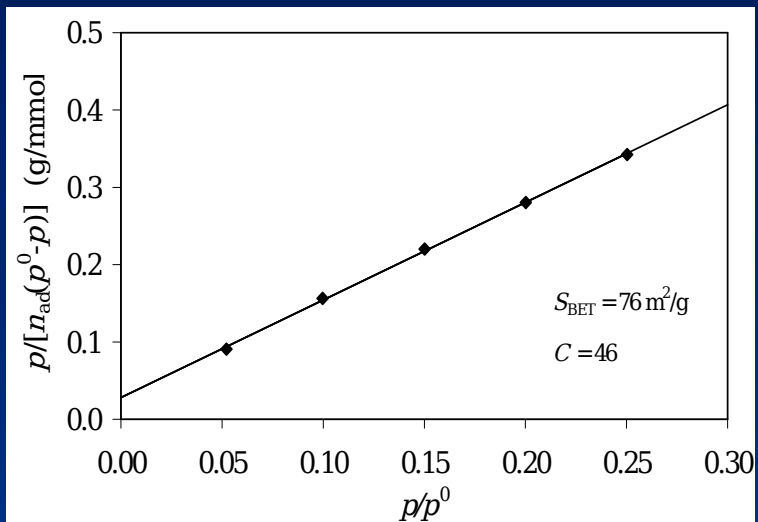


activated



BET- & *t*-plots

Raney Ni



ZSM-5

